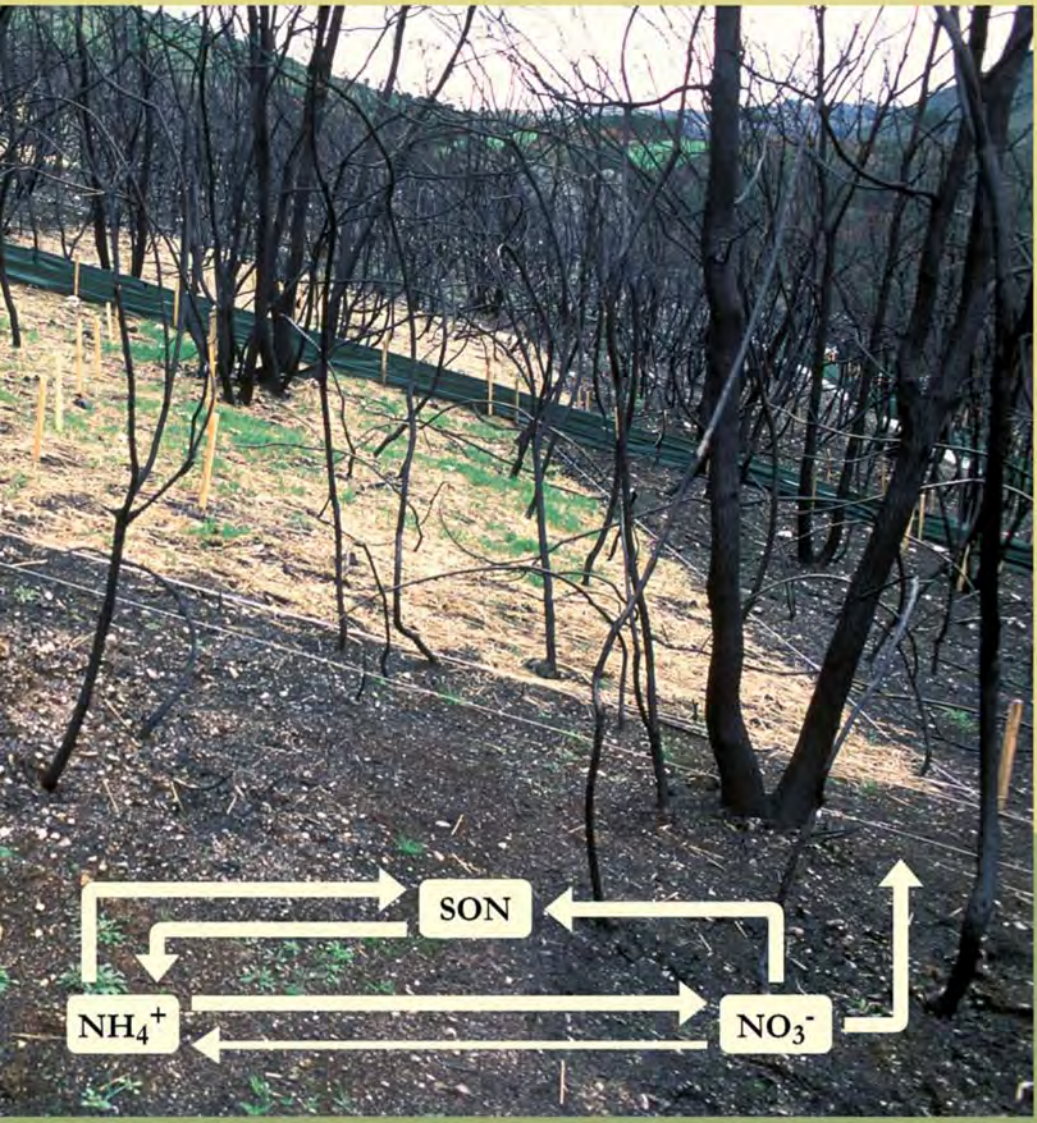
Impacts of fire, fire-fighting chemicals and post-fire stabilisation techniques on the soil-plant system



María Fernández Fernández
Universidade de Santiago de Compostela, 2017

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María Fernández Fernández

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Serafín J. González Prieto, Investigador Científico del Consejo Superior de Investigaciones Científicas, adscrito al Instituto de Investigaciones Agrobiológicas de Galicia, y Mª Xesús Gómez Rey

CERTIFICAN: Que la presente Memoria titulada «Impacts of fire, fire-fighting chemicals and post-fire stabilization techniques on the soil-plant system», presentada por la Licenciada en Biología María Fernández Fernández para optar al grado de Doctora en Biología, ha sido realizada en el Departamento de Bioquímica del Suelo, del Instituto de Investigaciones Agrobiológicas de Galicia, bajo su dirección y supervisión.

Que considerando que la presente Memoria constituye trabajo de Tesis Doctoral, autoriza su presentación en el Departamento de Edafología y Química Agrícola de la Universidad de Santiago de Compostela a fin de que pueda ser juzgada por el Tribunal correspondiente.

Y para que así conste a los efectos oportunos, firma la presente en Santiago de Compostela a 17 de febrero de 2017.

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Fdo.: Mª Xesús Gómez Rey

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Departamento de Edafoloxía e Química Agrícola

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Rosa Mª Calvo de Anta, Catedrática de Edafología y Química Agrícola de la Universidad de Santiago de Compostela, en su calidad de Tutora de la Licenciada en Biología María Fernández Fernández,

CERTIFICA: Que considerando que la presente Memoria titulada «Impacts of fire, fire-fighting chemicals and post-fire stabilization techniques on the soil-plant system» constituye trabajo de Tesis Doctoral, autoriza su presentación en el Departamento de Edafología y Química Agrícola de la Universidad de Santiago de Compostela a fin de que pueda ser juzgada por el Tribunal correspondiente.

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Fdo.: Rosa Mª Calvo de Anta

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"If soil is destroyed, then our liberty of choice and action is gone,
condemning this and future generations to needless privations and dangers."
(Walter C. Lowdermilk, 1953)

A Pepe,
que me enseñó tanto,
me contagió utopías
y esa actitud crítica
frente a la ciencia y la vida.

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Resumen

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Introducción

El suelo y el sistema suelo-planta

El concepto científico de suelo ha evolucionado profundamente desde que se comenzó a estudiar, y aun hoy no hay consenso absoluto en cómo definirlo. La FAO (Organización de las Naciones Unidas para la Alimentación y la Agricultura) lo define como un elemento natural que consiste en varias capas u horizontes compuestas de minerales meteorizados (45%), materia orgánica (5%), aire (25%) y agua (25%) (FAO, 2016a, b). La estructura del suelo, es decir, cómo se organizan en el espacio partículas, poros y organismos vivos, le confiere a éste una serie de propiedades (textura, estabilidad de los agregados, aireación, capacidad de retención de agua...) y funciones de vital importancia para el funcionamiento de los ecosistemas terrestres. Además de sus funciones ecosistémicas, los suelos también son la base de numerosos servicios ecosistémicos, aquellos bienes y servicios que los seres humanos obtenemos directa o indirectamente de los ecosistemas (Blaud et al., 2016; Costanza et al., 1997; Wall, 2012). El papel destacado que tienen los suelos en el funcionamiento del planeta se conoce desde hace relativamente poco, ya que hasta el siglo XX se consideraban exclusivamente como el medio sobre el que crecían las plantas (FAO y ITPS, 2015). El aumento de los impactos medioambientales causados por el ser humano también ha provocado una sensibilización creciente sobre la importancia de éstos. Por otro lado, la comunidad científica es cada vez más consciente de la interrelación entre elementos naturales que tradicionalmente se analizaban de forma independiente, y en este contexto, ha profundizado en el estudio de las funciones y servicios que prestan los suelos, así como de las principales amenazas que éstos sufren. Cada vez es más evidente que el suelo debería considerarse como un recurso no renovable desde la perspectiva temporal humana. Aunque en importantes instituciones internacionales como la FAO los suelos tienen una creciente relevancia en la agenda política y medioambiental, hay otras voces que defienden que los esfuerzos por visibilizar y paliar o remediar la degradación del suelo son insuficientes y no parten de la consciencia y actuación a nivel local.

La mayor parte de las plantas necesitan suelo para crecer y sobre la mayoría de los suelos del mundo crecen plantas. Las interacciones suelo-planta más importantes tienen lugar en la rizosfera, la zona alrededor de las raíces que está colonizada por una población de microorganismos muy específica y altamente influenciada por la actividad radicular (McNear Jr., 2013). Los intercambios de C orgánico, nutrientes minerales, agua y energía que tienen lugar en la rizosfera hacen de ella un componente fundamental para el desarrollo de cualquier suelo (Whitbeck y Cardon, 2007). A pesar de la aparente competición entre plantas y microorganismos por los nutrientes, ambos son interdependientes y se benefician mutuamente (Kuzyakov y Xu, 2013). Buenos ejemplos de estas relaciones simbióticas son las asociaciones entre bacterias del género *Rhizobium* y plantas leguminosas o de *Frankia* con plantas actinorrízicas para un proceso crucial del ciclo del N como es la fijación biológica de N_2; o las asociaciones entre algunos hongos y las raíces de muchas plantas vasculares (micorrizas), que parecen jugar un papel fundamental

en la estructura y funcionalidad de muchos ecosistemas terrestres y en la regulación de los ciclos del C y el N (van der Heijden et al., 2015).

Los suelos contienen más C que la atmósfera y la vegetación en conjunto, y por ello entender los mecanismos que regulan el C del suelo es fundamental para comprender el ciclo del C (Averill et al., 2014). Por otro lado, la disponibilidad de N en el suelo tiene una importante influencia en el ciclo del C porque limita las entradas de C al suelo provenientes de la producción primaria y las salidas de C asociadas a la actividad de los microorganismos del suelo (Averill et al., 2014). Además, el C exudado por las raíces puede desencadenar un incremento en la mineralización de N para satisfacer la demanda de la creciente población microbiana y por consiguiente la descomposición de la materia orgánica más recalcitrante del suelo (efecto "priming") (Bengtson et al., 2012; Blagodatskaya y Kuzyakov, 2008; Zhu et al., 2014). Modelos recientes proponen que el cambio global que está sufriendo el planeta tiene como consecuencia una importante alteración de los ciclos del C y el N; y en este escenario de cambio global aún no están claros el papel que juega el suelo (y la rizosfera en particular) en ambos ciclos biogeoquímicos y los posibles mecanismos de retroalimentación que se pueden desencadenar.

El ciclo del N

Se podría decir que en la naturaleza todo se recicla: el agua, la energía y los elementos están constantemente moviéndose y cambiando de estado en su paso por la atmósfera, la biosfera, la hidrosfera y la litosfera. Los ciclos biogeoquímicos del C, N y P están estrechamente relacionados como consecuencia directa de la vida, ya que estos tres elementos son componentes esenciales de los organismos vivos y su dinámica está conectada incluso a nivel molecular (Gruber y Galloway, 2008). Por ello, alteraciones en uno de estos tres ciclos pueden desencadenar mecanismos de retroalimentación en los otros dos (Lerman et al., 2004).

El N es uno de los nutrientes principales para los seres vivos (elemento fundamental de aminoazúcares, proteínas y ácidos nucleicos), pero la cantidad de compuestos de N disponibles en la naturaleza es muy reducida. Paradójicamente, el N es muy abundante en la atmósfera, pero sólo unos pocos microorganismos son capaces de romper el triple enlace de la molécula de N_2 gaseoso y convertirlo así en N disponible para el resto de seres vivos.

El conocimiento que hoy tenemos del ciclo del N es relativamente reciente. El elemento fue descrito por primera vez a finales del siglo XVIII, y la fijación biológica de N, uno de los procesos más importantes del ciclo, no se descubrió hasta finales del siglo XIX. Las sociedades en proceso de industrialización de aquella época se dieron cuenta de la limitación que suponía la falta de N disponible para satisfacer las necesidades de alimento de la creciente población humana, y la invención del proceso de Haber-Bosch (conversión de N_2 atmosférico a amonio) llegó justo a tiempo (comienzos del siglo XX). La fijación industrial de N permitió la fabricación de fertilizantes nitrogenados y el consiguiente aumento en la producción agrícola que permitió un sostenido ritmo de crecimiento poblacional. Sin embargo, este incremento en la producción de N reactivo ha resultado en la acumulación de éste en los ecosistemas, y esto a su vez está

generando una serie de efectos encadenados con repercusiones globales: aumento de los niveles de O_3 troposférico, alteración de la producción primaria terrestre y acuática, acidificación y eutrofización de las aguas y aumento del potencial de efecto invernadero de la atmósfera (Galloway et al., 2003).

Muchas de las transformaciones del ciclo del N terrestre tienen lugar en el suelo y están mediadas por microorganismos. El N_2 atmosférico puede ser fijado por rayos y luego depositado en el suelo (vía cuantitativamente poco relevante) o fijado por algunos microorganismos que viven, en general, en simbiosis con plantas. El N fijado entra en la cadena trófica y una vez muere el organismo vivo que lo asimiló, comenzará a descomponerse y convertirse en materia orgánica del suelo. Los microorganismos del suelo utilizan la materia orgánica como fuente de C, N y energía. Si la relación C/N de la materia orgánica es menor que la de los microorganismos que la están utilizando, éstos liberarán el exceso de N adquirido como NH_4^+ (mineralización de N orgánico o amonificación). Por el contrario, si la relación C/N es mayor, los microorganismos buscarán otras fuentes de N inorgánico (normalmente NH_4^+) inmovilizándolo. Ambos procesos son llevados a cabo por la mayoría de microorganismos del suelo y el balance entre ambos determina la cantidad de N inorgánico edáfico, que normalmente es mucho menor que la de N orgánico. Si el pH del suelo es elevado, el NH_4^+ se puede convertir en NH_3 y volatilizarse a la atmósfera, pero en general el NH_4^+ se oxida a NO_3^- en condiciones aeróbicas (nitrificación autótrofa). Como el NH_4^+ tiende a unirse a las partículas de suelo, pero el NO_3^- se pierde fácilmente por desnitrificación o por lixiviación, se podría decir que la nitrificación autótrofa regula la cantidad de N inorgánico que permanece en el suelo. El NO_3^- se puede convertir en N_2 y cerrar así el ciclo mediante el proceso de desnitrificación, cuya vía metabólica principal es la respiración anaeróbica que utiliza el NO_3^- como aceptor de electrones. Otra alternativa para el NO_3^- una vez absorbido por los microorganismos es su reducción enzimática a NH_4^+, aunque este proceso parece menos común que la nitrificación y la desnitrificación.

En el mundo industrializado y globalizado de hoy en día, hay que tener en cuenta el importante incremento en los aportes adicionales de N que son incorporados al suelo mediante fertilización y deposición de N inorgánico. El N asimilado por las plantas puede no volver al mismo ecosistema si las plantas son cosechadas, consumidas o quemadas. La lixiviación y la erosión, que pueden llegar a alcanzar una magnitud importante en ecosistemas degradados, conectan el ciclo terrestre y acuático del N y pueden resultar en importantes pérdidas de N de los suelos y eutrofización de los ecosistemas acuáticos.

Las tasas de mineralización neta son relativamente sencillas de medir y han sido ampliamente utilizadas como un índice de N disponible para las plantas (Schimel y Bennett, 2004). Sin embargo, la mineralización neta es el resultado de varios procesos simultáneos que se contrarrestan (mineralización bruta, inmovilización bruta y nitrificación bruta) y por lo tanto la cuantificación de estas tasas por separado proporciona una información mucho más valiosa sobre los mecanismos y dinámicas del ciclo del N en el suelo (Murphy et al., 2003; Rütting y Müller, 2007). Los métodos de cuantificación de las tasas brutas de transformación del N se basan en el principio de dilución y enriquecimiento isotópico de ^{15}N y se realizan mediante

incubaciones con trazadores marcados. El compartimento de N inicialmente marcado se va reponiendo con N no marcado según avanza la incubación, y los compartimentos no marcados se van enriqueciendo con el isótopo marcado según se va transformando el marcador (Mary et al., 1998; Stark, 2000). Midiendo el enriquecimiento en ^{15}N y cómo varía el tamaño de los distintos compartimentos de N a lo largo de la incubación, se pueden calcular las tasas brutas de transformación con métodos analíticos o numéricos (Murphy et al., 2003). Aunque las soluciones analíticas para calcular los flujos brutos de N continúan empleándose en escenarios sencillos, las soluciones numéricas proporcionan indudables ventajas (Murphy et al., 2003): 1) no hacen aproximaciones en los cálculos; 2) son aplicables a sistemas donde existe inmovilización simultánea de NH_4^+ y NO_3^-, remineralización o las cinéticas no son de orden cero; 3) permiten verificar la consistencia del conjunto de datos respecto al sistema modelizado; y 4) calculan todas las tasas simultáneamente, sin transmitir errores y toda la variabilidad al último flujo calculado, como sucede en los métodos analíticos. Entre las soluciones numéricas, el modelo *Ntrace* (Müller et al., 2007) es actualmente uno de los más avanzados. Los modelos numéricos consisten en una serie de ecuaciones diferenciales que se resuelven por métodos numéricos y rutinas de ajuste no lineal que buscan parámetros de las tasas que minimicen la función de coste entre los datos modelizados y el conjunto de datos observados (Müller et al., 2007; Murphy et al., 2003). La particularidad del modelo *Ntrace* es que utiliza un método de Monte Carlo por cadenas de Markov en combinación con el algoritmo de Metropolis para realizar un muestreo aleatorio por el espacio del modelo y evitar así quedar atrapado en mínimos locales. Esto permite una descripción de las transformaciones de N en el suelo más compleja y completa, porque se pueden estimar un mayor número de parámetros inequívocamente (Rütting y Müller, 2007).

Los incendios forestales

La Tierra es un planeta inflamable de por si ya que tiene cantidades suficientes de combustible (vegetación rica en C), agente oxidante (O_2 atmosférico) y abundantes fuentes de ignición (rayos y volcanes) (Bowman et al., 2009). Los incendios han afectado más superficie terrestre que cualquier otra perturbación natural y ocurren repetidamente en bosques tropicales, subtropicales, templados y boreales, así como en sabanas y áreas de cultivo en todo el mundo (Levine, 1991). Tanto el incendio de por si como los cambios que éste produce en la vegetación tienen importantes consecuencias en los ciclos biogeoquímicos, en el clima, en los rasgos evolutivos de muchos seres vivos, en la estructura y distribución de las comunidades vegetales y en muchos servicios ecosistémicos (Bowman et al., 2009; Lavorel et al., 2007; Pausas y Keeley, 2009). Además, se sabe que los regímenes del fuego y los impactos que éstos provocan son interdependientes con el clima, la estructura de la vegetación y el uso del suelo; y por ello la ecología del fuego es potencialmente muy sensible al cambio global (Bento-Gonçalves et al., 2012; Bowman et al., 2009; Lavorel et al., 2007).

Aunque el fuego es un fenómeno natural en la mayoría de los ecosistemas terrestres, hoy en día la mayoría de los incendios son provocados por el ser humano; ya sea directamente (incendios

intencionados, por accidente, negligencia o como efecto colateral de actividades humanas) o indirectamente por provocar un aumento de la vulnerabilidad de los ecosistemas al fuego (Blaud et al., 2016). Durante el siglo XX los regímenes del fuego en latitudes templadas han cambiado de forma drástica debido a importantes cambios en el uso del suelo (Pausas y Keeley, 2009). La industrialización conllevó un éxodo poblacional a las ciudades con el consiguiente abandono de las tierras de cultivo y de los pastos para el ganado, y el aumento del combustible vegetal en las zonas rurales (Pausas y Keeley, 2009). Además, se plantaron grandes extensiones de especies pirófitas como el eucalipto y el pino, y todo ello supuso un incremento en el número de incendios (Blaud et al., 2016; Pausas et al., 2008).

La terminología relativa a los efectos del fuego se utiliza a veces sin demasiada precisión y recientemente se ha planteado el debate de qué términos son los más adecuados. Así, la **intensidad del fuego** es la velocidad de liberación de energía en el incendio; la **severidad del fuego** se refiere a cómo la intensidad del fuego afecta al ecosistema y normalmente describe la cantidad de combustible y de materia orgánica consumida durante el incendio; las **respuestas del ecosistema** engloban todos aquellos procesos afectados por el fuego; y el **régimen del fuego** se refiere a las características comunes de los incendios que ocurren en un ecosistema determinado (Keeley, 2009; Neary et al., 2008; Vega et al., 2013a). Los incendios se pueden clasificar de acuerdo con diferentes criterios y no existe consenso en cuál es la clasificación más apropiada para predecir el amplio abanico de impactos ambientales causados por el fuego. Las clasificaciones tradicionales dividen los incendios en fuegos de superficie, de copa o subterráneos (Shakesby y Doerr, 2006); mientras que otras clasificaciones se basan en el régimen del fuego (Brown y Smith, 2000; Neary et al., 2008) o en indicadores visuales de la severidad del fuego (Vega et al., 2013b), siendo esta última propuesta la empleada en la presente tesis.

Los efectos del fuego sobre los ecosistemas son muy variados (Bowman et al., 2009), y es importante conocerlos para elegir y aplicar correctamente las medidas post-incendio adecuadas. En lo que respecta al aire, los principales impactos de los incendios son las emisiones de CO_2, CO, hidrocarburos, N_2O, NO_x y aerosoles (Crutzen y Andreae, 1990), dependiendo la cantidad emitida de los distintos gases de las características de cada incendio (Sandberg et al., 2002). Estas emisiones derivadas de los incendios tienen efectos a su vez en la visibilidad, las reacciones químicas que tienen lugar en la atmósfera, en los ciclos biogeoquímicos y en el clima (Alves et al., 2011). Aunque no existen muchos estudios sobre el tema, los incendios pueden producir emisiones incluso a largo plazo debido a las alteraciones que provocan en las propiedades del suelo. Por ejemplo, las elevadas concentraciones de N inorgánico en suelos quemados podrían fomentar las emisiones de N (Anderson y Poth, 1998; Dannenmann et al., 2011; Fierro y Castaldi, 2011; Inclán et al., 2012; Karhu et al., 2015); y el equilibrio suelo-atmósfera de CH_4 también podría verse afectado tras el fuego (Inclán et al., 2012).

El fuego y las actividades para la extinción de éste afectan en gran medida al ciclo hidrológico. Los principales impactos se derivan de la desaparición de la cubierta vegetal, que resulta en un mayor flujo de agua hacia el suelo; y de alteraciones en las propiedades del suelo, que conllevan una disminución de la infiltración y aumento de la erosión y escorrentía (Neary et al., 2008).

Todos estos cambios en las zonas quemadas normalmente provocan impactos importantes en diversas propiedades físicas, químicas y biológicas de los cursos y masas de agua, siendo las más severas aquellas relacionadas con los sedimentos y cenizas que se depositan en los ecosistemas acuáticos.

Los impactos del fuego sobre la fauna pueden ser directos (heridas, muerte, inmigración o emigración) o indirectos (i.e. equilibrios depredador-presa), cuando se derivan de los cambios en el hábitat provocados por el fuego (Smith, 2000). La magnitud de estos efectos depende del régimen del fuego y normalmente los efectos directos son menos acusados que los indirectos.

La vegetación es quizás la que sufre de forma más visible los efectos del fuego y, de hecho, muchas clasificaciones de incendios se basan en los daños sufridos por las comunidades vegetales (Couto-Vázquez, 2011). Las plantas tienen distintas estrategias de recuperación post-incendio: rebrotadoras obligadas, germinadoras obligadas, germinadoras facultativas (capaces de rebrotar y germinar), y especies colonizadoras (Pausas y Keeley, 2014). En zonas húmedas y fértiles, la revegetación después del incendio suele ser rápida y las especies rebrotadoras suelen desplazar a las germinadoras, ya que tienen la ventaja de disponer del espacio que previamente ocupaba la planta madura (Couto-Vázquez, 2011; Pausas y Keeley, 2014).

Los suelos también sufren de forma acusada el paso del fuego, dependiendo la magnitud y duración de los impactos de la severidad del fuego, su frecuencia y las condiciones meteorológicas post-incendio (Neary et al., 2008). Los principales efectos del fuego se pueden clasificar según la propiedad o proceso edáfico que se ve afectado:

- Propiedades físicas y químicas: debido a la deposición de cenizas y la combustión de la materia orgánica del suelo, el color de su capa superficial suele cambiar notablemente tras el incendio (Certini, 2005; Vega et al., 2013b). Por otro lado, el pH suele aumentar como consecuencia de la acumulación de cenizas y la desnaturalización de ácidos orgánicos; y la capacidad de intercambio catiónico disminuir por la combustión de gran parte de la materia orgánica (Certini, 2005). La destrucción de los agregados del suelo debida al fuego supone un cambio drástico en la estructura del suelo que suele conllevar una disminución de su capacidad de campo y un aumento del riesgo de pérdidas por erosión (Certini, 2005). En algunos incendios se origina una capa de suelo repelente al agua que también dificulta la infiltración y promueve la erosión (DeBano, 2000).

- Materia orgánica del suelo: es muy sensible al calentamiento, y su pérdida tanto en cantidad como en calidad después del fuego es quizás la consecuencia más destacada que los incendios provocan en el suelo, por lo importante que es ésta para la actividad biológica, la disponibilidad de nutrientes, la capacidad de intercambio catiónico, la estructura del suelo y la retención de agua (Certini, 2005; Neary et al., 2008).

- Nutrientes y elementos traza: al arder la vegetación, los nutrientes y elementos traza que ésta contenía se volatilizan o se depositan en el suelo con las cenizas y el material carbonizado. El suelo quemado suele presentar, de forma transitoria, elevadas

concentraciones de estos elementos; pero con el tiempo, las pérdidas por erosión o escorrentía pueden llevar a suelos empobrecidos con respecto a las condiciones de partida. En el caso del N, los principales efectos del fuego son: disminución de la cantidad total de N por volatilización, redistribución del N orgánico restante (aumento de compuestos recalcitrantes y disminución de los lábiles), conversión de N orgánico a NH_4^+ (combustión) y luego a NO_3^- (nitrificación), pérdidas por erosión y escorrentía, y la alteración significativa de las comunidades microbianas implicadas en el ciclo del N (Castro et al., 2006; Certini, 2005; Neary et al., 2008; Prieto-Fernández et al., 2004).

- Microorganismos del suelo: inmediatamente después del fuego la biomasa microbiana tiende a disminuir drásticamente o incluso sufrir una esterilización completa (Acea y Carballas, 1996; Barreiro, 2016; Certini, 2005; Díaz-Raviña et al., 1992; Díaz-Raviña et al., 1996). A pesar de este declive inmediato, los microorganismos que mineralizan la materia orgánica más lábil colonizan poco a poco los nichos vacíos y su actividad aumenta notablemente a corto plazo (Díaz-Raviña et al., 1996). Una vez agotada esta fuente de materia orgánica, las tasas de mineralización vuelven a disminuir y el total restablecimiento de las comunidades microbianas puede demorarse varios años (Barreiro, 2016).

- Erosión: aunque la erosión ocurre de forma natural en la mayoría de los ecosistemas terrestres, las numerosas perturbaciones producidas por el ser humano, entre las cuales está el fuego, tienen como consecuencia un aumento significativo en las tasas de erosión. La erosión provoca una disminución de la profundidad del suelo y sustrae grandes cantidades de nutrientes y materia orgánica, reduciendo la fertilidad del suelo y afectando a los cursos y masas de agua donde se deposita el material erosionado. Junto con los cambios en la vegetación, la erosión del suelo es el efecto del fuego más visible y dramático (Blaud et al., 2016; Neary et al., 2008). Las tasas de erosión post-incendio dependen en gran medida de la topografía, la geología, el clima, la cubierta vegetal que sobrevivió al fuego, las propiedades del suelo, etc., pudiendo llegar a suponer en algunos lugares más del 60% de la producción total de sedimentos (Neary et al., 2008). La erosión post-incendio puede ser parcialmente mitigada por alfombrados naturales que protegen el suelo como la deposición de cenizas, los restos no consumidos de la vegetación (hojas y acículas chamuscadas) o la vegetación que recoloniza la zona quemada (Robichaud et al., 2010).

Lucha integral contra los incendios

Las actividades de extinción de incendios, muy útiles para apagarlos rápida y efectivamente, pueden provocar impactos medioambientales significativos, que en algunos casos llegan a superar los efectos del fuego mismo (Backer et al., 2004). Una de las prácticas más comunes en regiones con alta recurrencia de incendios, es la aplicación aérea o terrestre de agentes retardantes de llama para incrementar la efectividad del poder extintor del agua. Los tres tipos principales de agentes retardantes de llama son (adaptado de Backer et al. (2004)):

- Espumas: sustancias químicas que inhiben la evaporación del agua y disuelven la cubierta cerosa de las plantas vivas, aumentando así la efectividad del agua y reduciendo la cantidad necesaria de ésta (Couto-Vázquez, 2011). Los productos que normalmente se comercializan son: Ansul Silv-Ex, Angus ForExpan S, Fire Quench, 3M Firebreak y, en España, Auxquímia RFC-88 (Couto-Vázquez, 2011). Aunque estos compuestos químicos pueden tener efectos negativos en los ecosistemas, no hay muchos estudios sobre el tema (Adams y Simmons, 1999; Larson et al., 1999; McDonald et al., 1996; Moody y Field, 2000) y la mayoría se centran en los daños a los ecosistemas acuáticos, dejando de lado los impactos sobre suelos y vegetación.

- Polímeros de poliacrilamida (Firesorb): aumentan la viscosidad del agua y su capacidad extintora. Además, pueden ayudar a mejorar la estructura del suelo e incrementar las tasas de infiltración (Basanta et al., 2002).

- Retardantes de llama a largo plazo: compuestos fundamentalmente de N y P, inhiben la combustión incluso cuando el agua se ha evaporado completamente (Couto-Vázquez, 2011). Las marcas comerciales que se usan normalmente son: Phos-Chek D75-F, Phos-Chek D75-R y Fire-Trol GTS-R, aunque en España el más utilizado es el FR Cross (Couto-Vázquez, 2011). A pesar de que la toxicidad de sus componentes base es baja (se suelen utilizar como fertilizantes), estos retardantes de llama también tienen importantes impactos en el medio ambiente: eutrofización de cursos de agua (Freedman, 1995), toxicidad directa para la flora y la fauna acuática (Gaikowski et al., 1996; McDonald et al., 1996; McDonald et al., 1997), y efectos sobre la vegetación terrestre (Bell et al., 2005; Bradstock et al., 1987; Couto-Vázquez et al., 2011; Cruz et al., 2005; Larson y Newton, 1996; Larson et al., 1999; Larson y Duncan, 1982; Luna et al., 2007; Song et al., 2014).

El aumento en el número de incendios y de la información disponible sobre los efectos deletéreos que éstos causan tanto en los ecosistemas como en infraestructuras humanas, ha provocado también un aumento en el uso de tratamientos post-incendio (Robichaud et al., 2010). En función de sus objetivos específicos y del momento de aplicación, estos tratamientos se dividen en tres tipos. Las acciones urgentes de estabilización post-incendio, llevadas a cabo durante el primer año, tienen como objetivo estabilizar la zona quemada; mientras que las actividades de rehabilitación y restauración se realizan a más largo plazo y persiguen mitigar los daños que probablemente no se restablecerían por sí solos. Las acciones urgentes de estabilización post-incendio se dividen a su vez en varias subclases (Napper, 2006), siendo objeto de esta tesis el alfombrado con paja o *"straw mulching",* uno de los tratamientos de ladera más efectivos para reducir la erosión post-incendio. Al cubrir el suelo quemado con paja, ésta reduce los efectos del impacto de la lluvia sobre el suelo desnudo, favorece la infiltración del agua y se crea un microclima que favorece la germinación del banco de semillas (Bautista et al., 2009; Robichaud et al., 2010). El principal inconveniente del alfombrado con paja es la introducción asociada de semillas no nativas, que pueden competir con las especies nativas de la zona quemada (Bautista

et al., 2009; Robichaud et al., 2010). Debido a su coste y las dificultades de aplicación, sólo se recomienda el uso del alfombrado con paja en zonas con un alto potencial erosivo que tengan, aguas abajo, zonas de alto valor ecológico o económico en riesgo (Bautista et al., 2009; Robichaud et al., 2010).

Para decidir si las acciones urgentes de estabilización post-incendio son necesarias o no y cuál es el tratamiento más adecuado, es necesario un temprano y minucioso estudio de las áreas quemadas que evalúe aspectos como la severidad del fuego, el clima, la topografía, el estado del suelo y de los cursos de agua y el riesgo que tienen los diferentes recursos de esa zona de sufrir daños (Napper, 2006). En la elección del tratamiento más adecuado hay que sopesar los costes y la efectividad del tratamiento considerado frente al potencial daño que causaría la erosión no mitigada (Robichaud, 2005). Afortunadamente, la cantidad de publicaciones que resumen las investigaciones sobre la efectividad de los distintos tratamientos y de informes técnicos que proporcionan información práctica sobre ellos crece constantemente y ayuda a una toma de decisiones más fundamentada que hace unos años (Bautista et al., 2009; Beyers, 2009; Moody et al., 2013; Napper, 2006; Parson et al., 2010; Peppin et al., 2010; Robichaud, 2005; Robichaud y Ashmun, 2013; Robichaud et al., 2010; Robichaud et al., 2013a; Robichaud et al., 2013b; Shakesby et al., 2016).

Contexto de la presente tesis

La mayor parte de la Península Ibérica pertenece al bioma mediterráneo (ecorregión mediterránea), mientras que la cornisa cantábrica, incluida Galicia, forma parte del bioma templado (ecorregión Eurosiberiana). La vegetación en Galicia es principalmente eurosiberiana, aunque debido al gradiente bioclimático que existe en la región, hay zonas y comunidades vegetales con una gran influencia mediterránea (Rodríguez Guitián y Ramil-Rego, 2007, 2008).

El paisaje gallego ha sufrido profundos cambios ya desde el Holoceno medio, cuando los bosques caducifolios climácicos fueron talados o quemados con distintos fines (producción de madera y carbón, conversión a pastos) y se expandieron los matorrales (principalmente *Ulex* spp. y *Erica* spp.) (Kaal et al., 2011). En las zonas rurales, estos matorrales se utilizaban como combustible y como cama para el ganado, que mezclado con el estiércol era un excelente fertilizante para las tierras agrícolas (Carballas, 2003). Sin embargo, a partir de mediados del siglo XX, este tipo de manejo agrícola sufrió grandes cambios: la madera se sustituyó por otros combustibles y el paso a sociedades más industrializadas conllevó un abandono de las prácticas ganaderas tradicionales y un incremento en el uso de fertilizantes inorgánicos. Además, se produjo una plantación masiva de eucaliptos y pinos, especies de crecimiento rápido, pero también pirófitas. En 50 años (1950-2000), Galicia incrementó su superficie forestal del 26% al 69% (Consellería do Medio Rural, 2016). Hasta los años 40 del pasado siglo, la mayor parte del territorio gallego era de propiedad privada, seguido de propiedad comunal y de un pequeño porcentaje de propiedad estatal o municipal. Sin embargo, después de la Guerra Civil, una gran parte de la propiedad

comunal fue expropiada por el Estado y reforestada; afectando gravemente a la ganadería extensiva y las economías locales, y provocando un descontento popular generalizado que a veces resultó en incendios intencionados. Este grave conflicto no se resolvió hasta los años 80, cuando se restableció la propiedad comunal. La población gallega está repartida por todo el territorio, aunque en las últimas décadas está sufriendo los procesos comunes a toda Europa de envejecimiento y éxodo rural; contribuyendo este hecho a los cambios antes mencionados en el uso de la tierra que a su vez explican parcialmente la alta incidencia del fuego en la región.

En España los incendios forestales, afectan cada año (especialmente en verano) a grandes superficies repartidas por todo el territorio nacional y suponen uno de los problemas ambientales más serios a los que se enfrenta el país. Según los datos proporcionados por el Ministerio de Agricultura y Pesca, Alimentación y Medio Ambiente, durante la década de 2001-2010 tanto el número de incendios como la superficie total quemada disminuyeron hacia el final del periodo, aunque los años 2005 y 2006 fueron especialmente dramáticos (Cubo María et al., 2012). La mayor parte de los incendios son causados por el ser humano (78% de los incendios, 83% del total de la superficie quemada), siendo el incendio intencionado la causa más común (50% de los incendios, 60% del total de la superficie quemada). Los motivos que llevan a los incendiarios a provocar el fuego suelen ser la quema de residuos agrícolas y la quema para la regeneración de pastos. Las especies forestales más afectadas por los incendios a nivel nacional son *Pinus pinaster*, *Pinus halepensis*, *Eucalyptus globulus* y *Quercus ilex*, tanto por ser las más abundantes como por ser más vulnerables al fuego.

Galicia, desde hace tiempo, es una de las regiones donde los incendios tienen una mayor incidencia: entre 1961 y 2011 hubo 250.000 incendios que quemaron 1.850.000 ha, casi dos terceras partes de la superficie total de Galicia. A pesar de representar un 6% de la superficie nacional, entre 2001 y 2010 Galicia sufrió el 42% de los incendios a nivel estatal y acumuló el 25% de la superficie total quemada. Los incendios intencionados son si cabe más comunes en Galicia (72% de los incendios frente al 55% de España).

El clima templado-húmedo, la abundante y densa vegetación de árboles y matorral y los horizontes de suelo bien desarrollados protegen con relativa eficacia a los ecosistemas gallegos de la erosión. Sin embargo, la situación cambia drásticamente tras los incendios y uno de los factores que más contribuye a las bajas tasas de erosión gallegas, el régimen de frecuentes precipitaciones que favorece la abundante vegetación y los profundos horizontes orgánicos en el suelo, se convierte en la principal amenaza para los suelos quemados en zonas de elevadas pendientes (Vega et al., 2013a). A pesar de que la precipitación abundante puede favorecer la aparición de una cubierta vegetal protectora en las zonas quemadas, el momento y la intensidad de los eventos de lluvia puede contribuir también a incrementar la tasa de erosión. Éste es el caso de Galicia, donde la mayoría de los incendios tienen lugar en verano, y las primeras lluvias del otoño, a menudo de corta duración pero intensas, tienen lugar cuando todavía no se ha regenerado la cubierta vegetal y desencadenan importantes pérdidas de suelo por erosión. Como la recurrencia de los incendios en Galicia es muy elevada, en las zonas que se ven afectadas por

el fuego repetidas veces las pérdidas de suelo por erosión son un grave problema que puede llegar a comprometer la fertilidad del suelo a más largo plazo (Vega et al., 2013a).

La recuperación post-incendio de la vegetación en Galicia se caracteriza por un aumento temporal (hasta los 2 años después del fuego) de la biodiversidad debido a la rápida colonización de herbáceas (Couto-Vázquez, 2011). La estrategia más común para el restablecimiento de las especies arbustivas es el rebrote de cepa. Es común que *Ulex europaeus, Erica arborea* y otras especies rebrotadoras o con semillas pirófitas dominen en zonas recurrentemente afectadas por incendios, mientras que especies germinadoras como algunas *Erica* spp. pueden llegar a ser desplazadas de las zonas quemadas (Couto-Vázquez, 2011). Las especies de árboles más afectadas por los incendios en Galicia son *Pinus pinaster* y *Eucalyptus globulus* (tanto por ser las más abundantes como por ser especies pirófitas); pero ambas son capaces de recolonizar rápidamente las zonas quemadas, ya sea a través de plántulas germinadas del banco de semillas (*Pinus pinaster*) o por rebrote (*Eucalyptus globulus*) (Couto-Vázquez, 2011).

La lucha integral contra los incendios debería incluir la prevención, la extinción, la evaluación de los efectos del fuego y la aplicación de tratamientos post-incendio en caso de ser necesarios; sin embargo, en Galicia está centrada casi exclusivamente en las actividades de extinción (Barreiro, 2016). Lamentablemente, los recursos destinados a la prevención de los incendios, ya sea a través de programas educativos o de labores de mantenimiento del territorio, y a la investigación de los efectos del fuego y de las acciones urgentes de estabilización post-incendio es más bien escasa. En Galicia, a partir del verano de 2006, que fue catastrófico en cuanto a incendios se refiere, se empezaron a invertir más recursos tanto en la investigación como en la implementación de los tratamientos urgentes de estabilización post-incendio (Vega et al., 2013a). Actualmente se dispone de un manual para evaluar de forma visual y rápida los impactos ocasionados por el fuego y para planear adecuadamente la implementación de los tratamientos necesarios (Vega et al., 2013a). También existen varios estudios que proporcionan valiosa información sobre la efectividad de distintas acciones urgentes de estabilización post-incendio repartidas por el territorio gallego (Díaz-Raviña et al., 2012; Gómez-Rey et al., 2013a; Gómez-Rey et al., 2013b; Gómez-Rey et al., 2014; Gómez-Rey y González-Prieto, 2014).

Objetivos y organización de la tesis

Hoy en día los incendios son una amenaza global para muchos ecosistemas, por los elevados daños económicos y ecológicos que provocan, entre ellos la destrucción de la vegetación y la degradación de los suelos. A nivel europeo, este problema es más grave en los países mediterráneos y en España alcanza, casi con más virulencia, a su zona templado-húmeda. Aunque las labores de extinción de incendios son fundamentales para una pronta y eficaz extinción de éstos, su coste económico es elevado y en algunos casos los impactos ambientales derivados de las labores de extinción son significativos e incluso llegan a superar a los del propio incendio. En Galicia los agentes retardantes de llama son ampliamente utilizados, a pesar de sus ya conocidos efectos

negativos en ecosistemas acuáticos y en organismos vivos y del desconocimiento de los efectos que estas sustancias químicas tienen en suelos y plantas.

Existen distintos tratamientos urgentes de estabilización post-incendio que desde no hace mucho se están aplicando en áreas severamente afectadas por el fuego para reducir la erosión y acelerar la regeneración natural de la vegetación. Uno de los tratamientos más habituales y efectivos en Galicia es el alfombrado con paja o *"straw mulching"*, aunque no se conocen los efectos que la incorporación de paja puede tener en, por ejemplo, los ciclos biogeoquímicos.

Para extinguir los incendios sin que ello perjudique aún más la zona afectada y para proteger los ecosistemas quemados de una potencial degradación posterior al incendio, es necesario evaluar cuándo y dónde se deben implementar estas medidas y optimizar su uso tanto a nivel de recursos empleados como de coste económico. En base a esto, los principales objetivos de la presente tesis, centrada en la región gallega, son:

- **Evaluar los efectos a largo plazo (10 años) del fuego y tres agentes retardantes de llama sobre el sistema suelo-planta (Sección 4).** Para ello, en julio de 2003 se realizó una quema controlada en Tomiño (Pontevedra), y se establecieron 5 tratamientos en un total de 20 parcelas: parcelas control sin quemar (US), parcelas control quemadas (BS) y parcelas quemadas con tres agentes retardantes de llama diferentes (agente espumante (BS+Fo), Firesorb (BS+Fi) y polifosfato amónico (BS+Ap)). Durante 10 años, se analizaron los efectos del fuego y los retardantes sobre propiedades del suelo (pH, concentración extraíble de nutrientes y elementos traza) y de la vegetación (cobertura, altura y contenido total de macronutrientes y elementos traza en las especies vegetales dominantes). Los resultados incluidos en esta tesis son los correspondientes a las muestras recogidas 10 años después de la quema.

- **Optimizar la técnica de protección de suelos quemados mediante alfombrado con paja ("mulching") para que sea económicamente viable, y evaluar los efectos de su aplicación en el sistema suelo-planta (Sección 5).** Para ello tras un incendio que tuvo lugar en Saviñao (Lugo) en septiembre de 2012, se diseñó una experiencia de campo con 12 parcelas experimentales con tres tratamientos: parcelas quemadas sin alfombrado de paja (BS) y parcelas quemadas con alfombrado de paja en franjas perpendiculares a la línea de pendiente anchas (WM, mayor dosis global) o estrechas (NM, menor dosis global). Tanto para los suelos como para los sedimentos erosionados se realizaron análisis de pH, nutrientes extraíbles y masa total de nutrientes (sólo sedimentos).

- **Evaluar los efectos del fuego, de la severidad del fuego y del alfombrado con paja sobre los flujos brutos de N en el suelo (Sección 6).** Al constar el ciclo del N de numerosos procesos que pueden verse afectados por el fuego de diferente manera, y también como consecuencia de la elevada heterogeneidad espacial de los efectos del fuego incluso en incendios de reducido tamaño; se consideró oportuno comenzar con experimentos en

condiciones controladas de laboratorio para evaluar de forma inequívoca los efectos del fuego y la adición de paja en los flujos brutos de N en el suelo. Para ello, después de un incendio en Vilameá (Ourense) en julio de 2014 se cogieron muestras del suelo quemado y de una zona no quemada adyacente de características similares y se establecieron tres tratamientos: suelo no quemado (US), suelo severamente quemado sin paja (BS) y suelo severamente quemado con paja (BSM). Se preincubaron las muestras durante 3 y 6 meses en condiciones óptimas de temperatura y humedad para acelerar la evolución de la mezcla suelo-paja y poder detectar los posibles efectos de ésta. Pasado ese tiempo, se realizaron incubaciones con ^{15}N y se estimaron las tasas brutas de transformación de N con el modelo *Ntrace*, uno de los más sofisticados disponibles hoy en día. Con el objetivo de aproximarse a las condiciones reales de campo, se planteó un segundo experimento con muestras procedentes de un incendio que tuvo lugar en el verano de 2015 en Palmés (Ourense) y se diseñó un experimento similar al anterior, pero que incluye dos importantes novedades: a) las preincubaciones de 3 y 6 meses se realizaron a la intemperie para aproximarse a condiciones reales de campo, y b) se incluyeron 5 tratamientos: suelo no quemado (US), suelo quemado (severidad media) con y sin paja (BIM y BI respectivamente), y suelo quemado (severidad alta) con y sin paja (BHM y BH respectivamente).

Materiales y métodos

Análisis de suelos y sedimentos

El suelo recogido en campo (y los sedimentos en el caso de la experiencia de Saviñao) se tamizó (< 2 mm) y se homogeneizó. Posteriormente, una parte se secó a temperatura ambiente para análisis de pH, nutrientes y elementos traza, y otra parte se conservó a su humedad de campo en la cámara fría para los análisis de N inorgánico y para las incubaciones con ^{15}N. En ambos casos, una pequeña alícuota de suelo se secó en la estufa a 105 ℃ durante 8 horas para determinar el contenido en agua del suelo. A su vez, una alícuota de las muestras de suelo seco se molió (< 100 μm) en un molino planetario con vasos y bolas de óxido de circonio para los análisis en el espectrómetro de masas. El pH se midió con un pH-metro por suspensión en agua y en KCl; la capacidad de campo se determinó con un equipo de plato-membrana de Richards a 10 kPa. Los nutrientes y elementos traza se extrajeron con NH_4Ac y DTPA y se cuantificaron mediante ICP-OES. El N inorgánico (NH_4^+ y NO_3^-) se cuantificó mediante extracciones con KCl y microdifusiones sucesivas. El N total y el $\delta^{15}N$ se determinaron, sobre muestras molidas, en un espectrómetro de masas acoplado a un analizador elemental.

En lo que respecta a los experimentos para estimar las tasas brutas del ciclo del N en los suelos de Vilameá, las muestras de suelo ya tamizado y homogeneizado se humectaron rápidamente hasta casi un 70% de su capacidad de almacenamiento de agua con ayuda de un humidificador ultrasónico, siguiendo la metodología de Gómez-Rey y González-Prieto (2013), ya empleada con éxito en suelos muy hidrófobos (suelos recién quemados y/o suelos ricos en materia orgánica y

muy secos). Una vez humectados los suelos, se aplicaron los distintos tratamientos (control no quemado con hojarasca, suelo quemado con y sin paja) y se colocaron en bandejas de plástico (20 x 20 x 2 cm) con pequeños agujeros para permitir el drenaje del exceso de agua. Las bandejas se cubrieron (sin sellar) con papel de aluminio para reducir la evaporación de agua y se mantuvieron durante 3 y 6 meses en una cámara en oscuridad a 25 ℃. Durante este tiempo, se ajustó regularmente la humedad de los suelos añadiendo alrededor de 20 ml de agua como si fuera lluvia. Después del periodo de preincubación, se realizó un experimento incubando las muestras en experiencias pareadas con $^{15}NH_4NO_3$ y $NH_4{}^{15}NO_3$, durante 1/2 hora, 1, 3 y 7 días. Se incubaron tres réplicas por cada combinación de tratamiento, trazador de ^{15}N y tiempo de incubación y en cada muestra incubada, se midieron las concentraciones de N-orgánico, N-$NH_4{}^+$ y N-$NO_3{}^-$ así como sus respectivas abundancias de ^{15}N.

En el caso de Palmés, los suelos, con su humedad de campo sin alterar, se dispusieron en bandejas similares a las del experimento anterior y se aplicaron los cinco tratamientos: control no quemado con hojarasca, suelo quemado (severidad media) con y sin paja, suelo quemado (severidad alta) con y sin paja. Las bandejas se dejaron a la intemperie durante 3 meses (octubre 2015 – febrero 2016) y 6 meses (octubre 2015 – mayo 2016) para simular las condiciones reales de campo. Para las incubaciones se utilizó un diseño experimental de doble marcaje con NH_4NO_3 similar al de Vilameá, pero se añadió un tiempo más de incubación (14 días), las muestras se incubaron a la temperatura media de la última semana de preincubación (9 ℃ preincubación de 3 meses y 14 ℃ preincubación de 6 meses), y en vez de cuantificar el N orgánico se cuantificó en N total de las muestras.

Análisis de vegetación

En el campo se midió la altura máxima y la cobertura de las especies de matorral dominantes (*Erica umbellata, Genista triacanthos, Pterospartum tridentatum, Ulex europaeus* y *Ulex micranthus*), así como la altura y el diámetro del tronco de los *Pinus pinaster* plantados 7 meses después de la quema prescrita. Las muestras foliares recogidas de *Erica umbellata, Pterospartum tridentatum, Ulex micranthus* y *Pinus pinaster* se lavaron, se secaron (60 ℃ durante 48 horas) y se molieron (< 100 μm) en el mismo molino utilizado para las muestras de suelo. El contenido total de nutrientes en el material vegetal se determinó sobre alícuotas de material molido y digerido en un microondas de alta eficacia durante 55 min y con HNO_3 al 65%. En el caso de las acículas de pino, se realizó además una digestion con HNO_3, HCl, y H_2O_2 en una placa calefactora para determinar el contenido total de P. Todas las muestras digeridas fueron analizadas mediante ICP-OES (procedimiento similar al explicado para los suelos).

Análisis estadísticos y modelos matemáticos

Los análisis estadísticos para los experimentos de Tomiño y Saviñao se realizaron con SPSS y se basaron principalmente en: ANOVAs de una vía (y las pruebas asociadas de normalidad, igualdad de varianzas y pruebas post-hoc para detectar diferencias entre grupos); y en PCAs.

Para cuantificar los flujos brutos de N en los suelos de Vilameá y Palmés, se utilizó el modelo *Ntrace*, uno de los métodos numéricos más sofisticados para estimar las tasas brutas del ciclo del N. La novedad de este modelo radica en la utilización de métodos de cadenas de Markov Monte Carlo (MCMC) en combinación con el algoritmo de Metropolis (MA) para aleatorizar la búsqueda de soluciones en el modelo y evitar llegar a mínimos locales, permitiendo así estimar un mayor número de parámetros y por lo tanto aportando una descripción más completa y compleja del ciclo del N en el suelo.

Principales resultados y conclusiones

Efectos del fuego y de los agentes retardantes de llama en el sistema suelo-planta (Sección 4)

En lo que se refiere a los suelos, diez años después de la quema prescrita, los suelos quemados tenían menos NO_3^- y más Mo que el control no quemado. Aunque las diferencias no fueron siempre significativas, las parcelas quemadas con adición de polifosfato amónico tenían los niveles más altos de P, Na y Al. El resto de variables analizadas para los suelos no presentaron diferencias importantes entre tratamientos.

Las plantas de las parcelas quemadas con adición de polifosfato amónico tenían los valores más elevados de $\delta\ ^{15}N$ (*P.pinaster* y *E. umbellata*), P (todas las especies), Na (*P. tridentatum* y *U. micranthus*) y Mg (*E. umbellata* y *P. tridentatum*). En el caso del K, las parcelas quemadas con polifosfato amónico presentaban los valores más altos para *P. pinaster* y los más bajos para las especies arbustivas (*E. umbellata*, *P. tridentatum* y *U. micranthus*).

Los pinos de las parcelas no quemadas tenían, en general, mayor altura y diámetro que los plantados en las pareclas quemadas. La única excepción eran los pinos de las parcelas quemadas con adición de polifosfato, donde se encontraron los pinos más altos y anchos, aunque la mitad de los individuos plantados estaban o muertos (parcelas con la segunda mortalidad más alta, después de las parcelas quemadas con adición de Firesorb) o tenían el tronco retorcido.

La adición de polifosfato amónico es el tratamiento que tuvo los efectos más acusados sobre la vegetación. En estas parcelas, *E. umbellata* presentaba los valores más bajos de cobertura y altura máxima, *U. micranthus* también valores muy bajos de cobertura y *P. tridentatum* el mayor porcentaje de cobertura. Además, éste fue el único tratamiento en el que no se encontraron ejemplares de *Genista triacanthos*, una especie que apareció en el área experimental 10 años después del fuego (y la exclusión del pastoreo) en el resto de parcelas.

La principal conclusión de este estudio es, por lo tanto, que el polifosfato amónico es el retardante con efectos más acusados y persistentes sobre suelos y plantas.

Optimización del alfombrado con paja (Sección 5)

Ninguna de las dos estrategias de aplicación de paja (franja ancha o franjas estrechas alternas) tuvo efectos significativos en la mayoría de las variables analizadas para suelos y sedimentos. El análisis de componentes principales muestra que las muestras de suelos y sedimentos, independientemente del tratamiento aplicado, cambian en función del tiempo después del incendio, disminuyendo progresivamente las diferencias entre muestreos consecutivos. Para los sedimentos, las variables pH_{KCl}, Ca, Mg, Mn y Zn se ajustan a modelos curvilíneos con el tiempo tras el fuego como variable independiente, mientras que el resto de variables no muestran una tendencia temporal clara. Durante el primer año post-incendio, se erosionaron algo menos de 500 kg ha^{-1} de sedimentos y el alfombrado con paja no tuvo ningún efecto en la masa total de sedimentos o de nutrientes perdidos por erosión.

De esta experiencia de campo se concluye que, debido a las precipitaciones moderadas que experimentó la zona de estudio aquel año, la tasa de erosión fue muy baja y por consiguiente el alfombrado con paja no pudo contribuir a reducir significativamente la magnitud de este proceso. Sin embargo, la concentración de Mo, Mn y Zn en los sedimentos excedía los niveles de referencia para la protección de ecosistemas y podría generar problemas de déficit en la vegetación de la zona afectada o problemas de toxicidad en los cursos de agua donde se depositen los sedimentos erosionados.

Efectos del fuego, de la severidad del fuego y del alfombrado con paja sobre los flujos brutos de N (Sección 6)

Incendio de Vilameá

Los resultados obtenidos indican que las tasas brutas de las distintas transformaciones del ciclo del N estimadas con el modelo *Ntrace* se ajustan bien a los datos experimentales. En los suelos preincubados durante 3 meses, se observa un pronunciado efecto del fuego en la tasa de mineralización de N orgánico (aproximadamente el doble) e inmovilización de NH_4^+ (tres veces mayor). El suelo cubierto con paja mostró valores intermedios entre el control y el suelo quemado sin paja para ambas tasas. La nitrificación autótrofa y la inmovilización de NO_3^- no se vieron afectadas ni por el fuego ni por la adición de paja. Mientras que en el suelo no quemado no se detectó nitrificación heterótrofa, en los dos tratamientos con suelos quemados se estimó una contribución de la nitrificación heterótrofa similar en magnitud a la inmovilización de NO_3^- y a la nitrificación autótrofa.

En los suelos preincubados durante 6 meses no se encontraron diferencias entre tratamientos en la mineralización de N orgánico e inmovilización de NH_4^+; pero los dos suelos quemados

presentaban una nitrificación autótrofa casi 10 veces superior al control. La inmovilización de NO_3^- también era mayor en los suelos quemados (3-4 veces superior). Al igual que a los 3 meses, sólo los suelos quemados presentaban nitrificación heterótrofa. La adición de paja no tuvo efectos apreciables en ninguna de las tasas estimadas en los suelos preincubados durante 6 meses.

A la vista de estos resultados, se puede concluir que el fuego afecta notablemente el ciclo del N en el suelo, favoreciendo primero la producción de NH_4^+ (preincubación de 3 meses) y su posterior transformación en NO_3^- (preincubación de 6 meses). Si en condiciones de campo los suelos quemados se comportan de forma similar, las elevadas tasas de nitrificación pueden resultar en pérdidas de NO_3^- por lixiviación o desnitrificación si se dan las condiciones adecuadas. Ambos procesos supondrían una pérdida de N en el ecosistema quemado y la eutrofización de las aguas en el caso de que se produjera lixiviación o la producción de gases de efecto invernadero (NO y N_2O) si ocurre la desnitrificación. Este experimento aporta evidencias de que, en condiciones de laboratorio, la adición de paja resulta en efectos intermedios a corto plazo entre el suelo control y el quemado sin paja en cuanto a las tasas de mineralización de N orgánico e inmovilización de NH_4^+ se refiere, y ausencia de ellos en el más largo plazo.

Incendio de Palmés

Los resultados del experimento de Palmés indican que, al cabo de 3 meses de preincubación, en US la mineralización de N orgánico, la inmovilización de NH_4^+, la nitrificación heterótrofa y la desnitrificación eran un orden de magnitud mayor que la nitrificación autótrofa y la reducción no asimiladora de nitrato (DNRA); sin embargo, a los 6 meses, la mineralización de N orgánico y la inmovilización de NH_4^+ se mantuvieron parecidas, pero la nitrificación heterótrofa, la DNRA y la desnitrificación aumentaron y la nitrificación autótrofa disminuyó ligeramente. A los 3 meses, los suelos quemados de alta severidad no presentaban nitrificación heterótrofa, la mineralización de N orgánico y la inmovilización de NH_4^+ eran menores que en US, la nitrificación autótrofa era la tasa con valores más altos y la desnitrificación en BHM era aproximadamente el doble que en BH. A los 6 meses la mineralización de N orgánico, la inmovilización de NH_4^+ y la desnitrificación aumentaron (tasas de desnitrificación más altas de todo el experimento), la nitrificación autótrofa disminuyó levemente, y la nitrificación heterótrofa apareció en BH. Por el contrario, los suelos moderadamente quemados, presentaban a los 3 meses, tasas de mineralización de N orgánico, inmovilización de NH_4^+ y nitrificación autótrofa más elevadas en comparación con US, y menos nitrificación heterótrofa y desnitrificación. A los 6 meses, una nueva tasa (mineralización de N orgánico recalcitrante) apareció en BI y BIM, pero estos suelos presentaron ciclos del N muy diferentes: en BI el patrón fue muy similar a BH y BHM, pero en BIM la mineralización de N orgánico y la inmovilización de NH_4^+ disminuyeron notablemente, la desnitrificación desapareció, la DNRA disminuyó y la nitrificación heterótrofa aumentó.

En base a los resultados del experimento de Palmés, se puede concluir que el impacto causado por la severidad del fuego en la calidad y cantidad de materia orgánica, así como

en las comunidades microbianas del suelo, afecta a su vez a las tasas de mineralización de N orgánico e inmovilización de NH_4^+. A corto plazo (3 meses), ambas tasas se incrementaron sustancialmente en los suelos quemados de media intensidad, mientras que en los quemados de alta intensidad este aumento no se produjo hasta los 6 meses. Además, el incremento en la mineralización-inmovilización combinado con la elevada humedad del suelo probablemente limitaron la actividad de los nitrificantes autótrofos y promovieron tanto la DNRA como la desnitrificación debido a la competición por el substrato (NH_4^+) y a la disminución de los niveles de O_2. Los suelos severamente quemados presentaban, al cabo de 6 meses, las tasas de desnitrificación más altas de todo el experimento, aunque la baja relación nitrificación autótrofa/inmovilización de NH_4^+ sugiere que esa desnitrificación tan elevada quizás no se fuera a sostener mucho más tiempo. Cabe destacar que es la primera vez que se describe la existencia de DNRA en suelos quemados, siendo su magnitud similar a la del control no quemado. La contribución relativa de la DNRA y la desnitrificación al consumo de NO_3^- en suelos quemados puede tener importantes implicaciones en la retención de N en el suelo y en la emisión de gases de efecto invernadero. El alfombrado con paja no tuvo un efecto apreciable en los suelos severamente quemados, pero en los quemados de media intensidad la adición de paja produjo un aumento de la mineralización-inmovilización, la desnitrificación y la DNRA; además, afectó negativamente a la nitrificación autótrofa a corto plazo, seguramente debido al aporte extra de materia orgánica. A los 6 meses, las plantas crecidas en el suelo moderadamente quemado con paja probablemente competían con los microorganismos por el N y otros nutrientes disponibles y aportaban exudados radiculares capaces de inhibir parcialmente la mineralización-inmovilización y la desnitrificación.

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Section 1

Introduction

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1.1 Soils

"Essentially, all life depends upon the soil. There can be no life without soil and no soil without life; they have evolved together." (Charles E. Kellogg, 1938)

1.1.1 Definition, formation and functions

The word "soil" has different meanings to different people; and although it is a quite familiar term for all of us - we step on it every day -, it is not easy to define what soil is. As Bockheim et al. (2005) claim, the understanding of currently accepted concepts often requires knowledge of how the ideas that led from one concept to another have evolved with time, and therefore they have traced the historical evolution of the soil concept. The earliest attempts (19^{th} century) defined the soil as a weathered rock layer that serves as medium for plant growth. From then on, new concepts such as soil as a natural body, soil-forming factors and co-evolution of soils and landforms, were incorporated to the soil definition. Nowadays, although there is no unique definition of soil, all these fundamental concepts are taken into account and soil is defined, for example, as the result of the interactions between the atmosphere, the biosphere and the geosphere (Blaud et al., 2016). The Food and Agriculture Organisation of the United Nations (FAO) defines soil as a natural body consisting of layers (soil horizons) that are composed of weathered mineral materials, organic material, air and water; or as the end product of the combined influence of climate, topography and organisms (including humans) on parent materials (original rocks and minerals) over time (FAO, 2016a). In other words, soil is any loose material on the Earth's surface that is capable of supporting life; or in a more poetic way, we can say that soil is the skin of our planet, and as our skin, it is fully alive and always breathing.

On average, soils are made up of minerals (45%), water (25%), air (25%) and organic matter (5%) (FAO, 2016d), but soils are much more than all these elements put together: soil is an incredibly complex and diverse organisation of pores, particles and living organisms. These three entities – "bricks, rooms and architects/dwellers" – constitute the pillars of basic soil functions and are mutually dependent: soil properties are greatly shaped by soil biota and, vice versa, soil biodiversity is distributed and organized upon soil's structure and composition. Soil aggregates – the "bricks" - consist of mineral and organic materials bound together and are generally defined by their size and their physical and chemical properties. Whereas the nature of soil mineral particles determines soil texture, soil organic matter (SOM) - a complex mixture derived from plant litter and microbial products in all stages of decomposition - improves soil aggregate stability and plays a key role in soil structure and functioning. Soil pores - the "rooms" of the ecosystem - provide aeration and hold different amounts of water, allowing soil organisms to respire and supplying them the precious liquid. Last but not least, there are soil organisms, the "architects" and "dwellers" of the soil. As stated in Blaud et al. (2016), *"let the organisms organise their habitat and soil will start to exist"*. Soil is teeming with life: nowhere in nature are living organisms – from microorganisms to fauna and flora - so densely packed as in soils. Some

illustrative examples: one gram of soil may have millions of individuals and several thousand species of bacteria, or one tablespoon of healthy soil contains more organisms than the planet's entire human population. Soils are widely recognized as a key reservoir of global biodiversity (they host a quarter of the planet's diversity) and soil biodiversity has a fundamental role in supporting soil functions and therefore in providing ecosystem goods and services associated with soils.

Soils can be just a few centimetres deep or up to 190 m, and it can take from around 100 years to get 2-5 cm of soil, up to 5000 years to produce just 1 cm (Blaud et al., 2016). Soil formation is a long and complex process that greatly determines the properties of each soil on Earth and it is triggered by the weathering and erosion of the bedrock. Parent material, topography, climate, time, living organisms and human activities are the main soil forming factors that determine the speed, type and extent of weathering. Consequently, the enormous geographical diversity of soil types is greatly explained by all the possible combinations of the soil forming factors across the world.

Soils play a crucial role in the well-functioning of all terrestrial ecosystems and they also provide social and economic services that are vital to humans, nonetheless the terms ecosystem (or soil) "functions" and "services" are often confused. Ecosystem functions refer to the biological, geochemical and physical components and processes within ecosystems, whereas ecosystem services (for simplicity the term encompass both goods, such as food, and services, such as waste assimilation) are the tangible and intangible benefits that humans obtain, directly or indirectly, from ecosystems (Blaud et al., 2016; Costanza et al., 1997; Wall, 2012). Soils have a large number of functions, while ecosystem services have been divided into four broad classes: provisioning, regulating, supporting, and cultural services (Millennium Ecosystem Assessment, 2005). It should be beard in mind that many ecosystem functions are interdependent among them, and also that ecosystem services and functions do not necessarily show a one-to-one correspondence (Blaud et al., 2016; Costanza et al., 1997). In FAO and ITPS (2015) ecosystem services and the specific soil functions that enable those services are summarized in Table 1.1.

Table 1.1: Ecosystem services provided by the soil and the soil functions that support these services (from FAO and ITPS (2015)).

Ecosystem service	**Soil functions**
Supporting services: Services that are necessary for the production of all other ecosystem services; their impacts on people are often indirect or occur over a very long time.	
Soil formation	Weathering of primary minerals and release of nutrients. Transformation and accumulation of organic matter. Creation of structures (aggregates, horizons) for gas and water flow and root growth. Creation of charged surfaces for ion retention and exchange.
Primary production	Medium for seed germination and root growth. Supply of nutrients and water for plants.
Nutrient cycling	Transformation of organic materials by soil organisms. Retention and release of nutrients on charged surfaces.
Regulating services: benefits obtained from the regulation of ecosystem processes.	
Water quality regulation	Filtering and buffering of substances in soil water. Transformation of contaminants.
Climate regulation	Regulation of CO_2, N_2O, and CH_4 emissions.
Erosion regulation	Retention of soil on the land surface.
Provisioning Services: products ('goods') obtained from ecosystems of direct benefit to people.	
Food supply	Providing water, nutrients, and physical support for growth of plants for human and animal consumption.
Water supply	Retention and purification of water.
Fibre and fuel supply	Providing water, nutrients, and physical support for plant growth for bioenergy and fibre.
Raw earth material supply	Provision of topsoil, aggregates, peat etc.
Surface stability	Supporting human habitations and related infrastructure.
Refugia	Providing habitat for soil animals, birds etc.
Genetic resources	Source of unique biological materials.
Cultural services: nonmaterial benefits which people obtain from ecosystems through spiritual enrichment, aesthetic experiences, heritage preservation and recreation.	
Aesthetic and spiritual	Preservation of natural and cultural landscape diversity. Source of pigments and dyes.
Heritage	Preservation of archaeological records.

1.1.2 Soil threats

"A nation that destroys its soils destroys itself." (Franklin D. Roosevelt, 1937)

Our views about the Earth beneath our feet have evolved throughout history, so have changed the way humans have managed it. Different ways of soil exploitation and management are behind the rise and fall of many ancient civilisations and soils continue to support the needs of contemporary societies (Wall, 2012). Until the 20th century, soil was considered almost exclusively as the basis of agriculture and food production (FAO and ITPS, 2015). As the

global human impact on the environment increases, so does our awareness of environmental issues and research on the topic has grown substantially in the last decades. The scientific community is now unravelling the wide range of ecosystem services provided by soils and all the pressures threatening them, as well as the connections between soil and broader environmental concerns.

Soil degradation leads to the destruction of the functionality and resilience of managed and natural ecosystems (Bouma and McBratney, 2013). The Soil Protection Strategy approved in 2006 by the European Union (see Bouma and McBratney (2013)) defined as the main threats to soil: erosion by water and wind, organic matter decline, compaction, salinization, landslides, soil sealing and soil contamination. Conversely to other environmental issues (e.g. climate change), soil threats can be well observed and defined in terms of causes and effects (permanent for erosion and often of very long duration for degradation) (Bouma and McBratney, 2013). Although soils seem to be inexhaustible, we are becoming aware that they should be considered as a non-renewable resource from a human time perspective.

However, soil degradation is only one more of the several environmental issues humankind is facing nowadays. Lately, the concept of planetary boundaries as the safe limits outside which the Earth system cannot continue to function in a stable state has been suggested as a helpful tool to prevent human activities from causing unacceptable environmental change (Rockstrom et al., 2009). There are nine such processes for which planetary boundaries should be established: climate change, rate of biodiversity loss, interference with the N and P cycles, stratospheric ozone depletion, ocean acidification, global freshwater use, change in land use, chemical pollution, and atmospheric aerosol loading, being the safe boundaries of the first three already crossed (Rockstrom et al., 2009). Similarly, six main global environmental challenges for sustainable development have been recently recognized: food, water and energy security, climate change abatement, biodiversity protection and ecosystem service delivery (Bouma and McBratney, 2013; McBratney et al., 2014). These publications also highlight the key role soils play in the global environmental sustainability challenges (most of them are land-related issues) and suggest the metaphor of soils as a keystone connecting the various environmental issues mentioned above (Fig. 1.1).

According to this view, the international community is gradually giving more priority to soil related issues and approaching the topic from different perspectives. A good example is the Soil Carbon Initiative (2011), where the term "soil security" was suggested as an alternative to soil quality, soil health or soil protection, as it has a wider and more integrative meaning. It is a similar concept to food, water or energy security and refers to *"the maintenance or improvement of the world's soil resource so it can provide sufficient food and fibre, fresh water, contribute to energy sustainability and climate stability, maintain biodiversity and overall environmental protection and ecosystem services"* (Soil Carbon Initiative, 2011). Moreover, trying to enhance collaboration and synergy of efforts between all stakeholders (from land users through to policy makers) the Global Soil Partnership (GSP) was founded in December 2012 hosted by the FAO. At its first Plenary Assembly, the Intergovernmental Technical Panel on

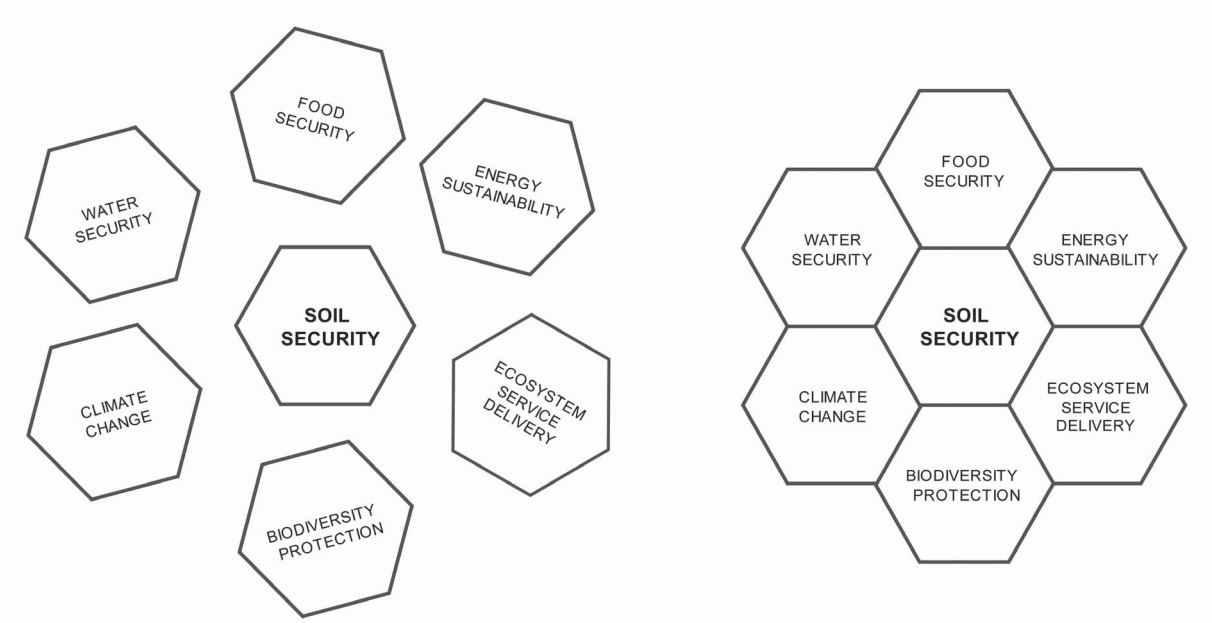

Figure 1.1: Major land-related environmental issues that, when considered together and not independently, provide researchers a more comprehensive characterisation of the Earth and the current environmental challenges (adapted from Bouma and McBratney (2013)).

Soils (ITPS) was established to provide the partnership scientific and technical advice and guidance on global soil issues. In 2015, coinciding with the International Year of Soils, the ITPS prepared the revised version of the World Soil Charter (WSC) to promote and institutionalize sustainable soil management; and produced the Status of the World's Soil Resources report (FAO and ITPS, 2015), aimed at scientists, laymen and policy makers, to make clear the essential connections between soils and human activities. Both documents stress the key role of soils, how human pressure on them is reaching a critical threshold and the importance of sustainable soil management to revert this scenario.

Despite all these FAO initiatives, other voices claim that there is a lack of interdisciplinary studies, vital for addressing global environmental issues, and that many international reports do not mention yet the role of soils (Bouma and McBratney, 2013; Stiftung, 2015). Moreover, many declarations and proposed action programs have neither achieved an increased public awareness nor an effective political action (Bouma and McBratney, 2013; Stiftung, 2015). Unfortunately, as human labour devoted to working the land has steadily decreased, most people have lost contact with the soil understood as the base for food production and regulator of many environmental processes; and the dialogue between the soil science community and the general public is rather scarce (FAO and ITPS, 2015). Bouma and McBratney (2013) wonder how the soils can be placed on the international policy agenda and how to convince the public and the policy arena of the "value" of something that is difficult to express in monetary terms, and they analyse the role soil scientists may play in spreading the importance of soils in the current global change scenario. They warn about the communication problems that might arise when senders of information

are so convinced of the significance of what they have to say, that they pay no attention to the opinions of the intended receivers of such information, who often have quite different beliefs and in the end are the ones determining whether or not the sender's message is received. In the authors' opinion, we need knowledge brokers, people who are able to inject the right type of knowledge to the right kind of people at the right time and in the right way. Furthermore, as the implementation of soil management decisions is typically made locally and occurs within widely differing socio-economic contexts, environmental initiatives should be co-designed by the different stakeholders involved, giving special importance to local and indigenous knowledge (Bouma and McBratney, 2013; FAO and ITPS, 2015).

1.1.3 The soil-plant system

Most plants on Earth need soil to grow and most soils in the world have plants growing on them. Soils support plant growth by providing plants with nutrients, acting as a water holding tank and serving as the substrate to which plants anchor their roots; on the other hand, vegetation prevents soil degradation and desertification by stabilizing the soil, maintaining water and nutrient cycling, and reducing water and wind erosion (FAO, 2016c). Most interactions between soil and plants take place within the soil-root interface (rhizosphere), the area around plant roots that is inhabited by a unique population of microorganisms influenced by root growth and activity (McNear Jr., 2013). The rhizosphere is not a region of definable size or shape, but instead consists of a gradient of substrate availability, water potential and redox state and it can be considered both a crossroads and a marketplace (Hawkes et al., 2007; Whitbeck and Cardon, 2007). The influence of rhizosphere processes extends far beyond the rhizosphere itself as the exchange and transformation of universal biological currencies (organic C, mineral nutrients, water and energy) taking place in it determine community structure and ecosystem properties (Whitbeck and Cardon, 2007). In fact, some authors claim that the rhizosphere is such a fundamental driver of overall soil development that all soil might be viewed as rhizosphere soil of varying age (Whitbeck and Cardon, 2007).

Competition for available nutrients between plants and microorganisms is particularly strong in the rhizosphere, where nutrient limitation is greater than in the non-rhizosphere soil (Kuzyakov and Xu, 2013). Despite this apparent competition, microorganisms and roots are mutually dependent and coexist and benefit from each other, being the mechanisms of this coexistence still unclear (Kuzyakov and Xu, 2013). In the case of N, these authors hypothesize that competitive and mutualistic interactions develop mainly on the basis of temporal and spatial niche differentiation for N acquisition and that the fast uptake of N by microorganisms together with its subsequent slow release: a) is an important adaptation of ecosystems against possible N losses; b) probably affects plant species competition (plants associated with rhizosphere microorganisms may use them as a N source); and c) continuously provides roots with available N according to plant demand.

Good examples of symbiosis between plant roots and microorganisms are the symbiotic N_2-fixing association between rhizobia and leguminous plants and between *Frankia* and actinorhizal plants, as well as the association of some fungi and the roots of some vascular plants (mycorrhizae). Although the physiology of symbiotic N_2 fixation is reasonably well characterized, our understanding of its ecological control is limited to a few cultivated ecosystems (Vitousek et al., 2002a). Whereas this symbiotic N_2-fixing association is restricted to certain plant families (Stacey et al., 1992), almost all land plants form symbiotic associations with mycorrhizal fungi (van der Heijden et al., 2015). The amount of resources that can be moved above or below ground by the ubiquitous mycorrhizal symbiosis suggests that mycorrhizae play a key role in terrestrial ecosystems, regulating nutrient and carbon cycles and influencing soil structure and ecosystem functionality (van der Heijden et al., 2015). A recent theoretical model suggests that competition for limiting nutrients such as N between the different types of mycorrhizal fungi and free-living microorganisms is what determines the rate of C decomposition and storage in soils (Orwin et al., 2011). That means that mycorrhizal status rather than climate variables, net primary production or clay content would exert a greater control over soil C content (Averill et al., 2014). For instance, Clemmensen et al. (2013) and Clemmensen et al. (2015) provide evidence that in boreal forests - a terrestrial net sink of C -, long-term ecosystem succession and humus build-up is accompanied by phylogenetic and morphological shifts in the mycorrhizal fungal community with potential consequences for C and N cycling. They suggest that these fungal community changes are important to explain the large accumulation of organic matter belowground often observed in older ecosystems and that aboveground plant litter dynamics on its own cannot explain this phenomenon.

Soil contains more C than the atmosphere and vegetation together, and thus understanding how this C pool is regulated is crucial to fully understand the C cycle (see Averill et al. (2014), Dungait et al. (2012) and references therein). Nearly half of total soil respiration comes from SOM decomposition, a process strongly regulated by the rhizosphere through root exudates and microbial activity changes (Zhu et al., 2014). The term priming effects refers to an increase in the rate of SOM decomposition driven by increased plant rhizodeposits of easily available C or N (Bengtson et al., 2012; Blagodatskaya and Kuzyakov, 2008; Zhu et al., 2014). Although it is still under debate, a possible explanation of the priming effect is that the increased rhizodeposition of C substrates enhances microbial growth and extracellular enzyme production and, as a result, it promotes the decomposition of more recalcitrant SOM (Zhu et al., 2014). As organisms require C and N in strict proportions, both biogeochemical cycles constrain each other: N availability can limit C inputs to the soil from net primary production and C outputs associated with the activity of soil microorganisms (Averill et al., 2014); but also the labile C exuded by roots may trigger an increase in N mineralisation in soils with low N availability to meet the N demand of the growing microbial population (N mining effect) (Garcia-Pausas and Paterson, 2011; Zhu et al., 2014).

Increasing awareness of global change, and in particular of the important alterations of the C and N cycles, have drawn attention to belowground processes and their role in global C and

N dynamics. As interactions of plants and soil microorganisms are fairly specific, have positive evolutionary traits and rhizospheric processes play a key role in C and N dynamics, alterations on either the plant community or the soil system would impact global biogeochemical cycles. Recent conceptual models state that elevated atmospheric CO_2 concentrations and increased atmospheric N deposition modify plant C allocation and trigger a response in the rhizosphere altering its food webs and the rates of C and N cycling (Clemmensen et al., 2013; Pregitzer et al., 2007). Elevated atmospheric CO_2 concentrations are supposed to be partially mitigated by a higher primary production and subsequent C sequestration in plant biomass and SOM (Bengtson et al., 2012). However, higher CO_2 concentrations and warmer temperatures can also enhance SOM decomposition and whether this balance results in a net positive or negative feedback to rising CO_2 atmospheric concentrations remains unclear (Garcia-Pausas and Paterson, 2011). Furthermore, it is paramount to understand whether soil N availability will increase, decline or remain unchanged to ascertain if initial enhancement of net primary production will be sustained in the long term (Pregitzer et al., 2007).

1.2 The nitrogen cycle

"The nitrogen cycle poses many challenges. None of these is more fundamental than the question: Why is the supply of N so important to the functioning of many terrestrial and aquatic ecosystems?" (Peter M. Vitousek, 2002)

Nature is all about cycling: energy, water and elements are constantly moving and changing its state through the different Earth compartments (atmosphere, biosphere, hydrosphere and lithosphere). Life is possible thanks to this continuous cycling of energy and matter, but living organisms also play a crucial role in the biochemical cycles. The magnitude of the cycling of elements within ecosystems is rather large and it dwarfs the amount provided by the atmosphere or rock weathering (Schlesinger and Bernhardt, 2013a). This large "internal" cycling is achieved by the long-term retention and recycling of the elements: important biochemical elements are accumulated within ecosystems by biotic uptake, whereas nonessential or non-limiting elements pass through these systems under simple geochemical control (see Schlesinger and Bernhardt (2013a) and references therein).

Biogeochemical cycles of C, N and P are tightly coupled as a direct consequence of life; these elements are essential constituents of living organisms and therefore their dynamics are already linked at the molecular level (Gruber and Galloway, 2008). How tight the coupling between cycles is, as well as the relative speed at which the cycles are coupled, it is determined by the elemental stoichiometry (Gruber and Galloway, 2008). Whereas the C:N:P Redfield ratios for aquatic primary producers are within a rather narrow range, estimates for the land phytomass and soil humus are more variable (Lerman et al., 2004). The strong coupling between biogeochemical cycles also implies that alterations in one of them can trigger feedback mechanisms in the others. Lerman et al. (2004) define four human-borne forcings that have been increasingly altering

biogeochemical cycles in the last 300 years: fossil fuel burning, land use change, application of chemical fertilizers on land, and organic sewage discharge.

Although N is the most abundant of the essential elements for life in Earth's atmosphere, hydrosphere and biosphere, it is the least readily available for living organisms (Galloway et al., 2003). Nitrogen is one of the main nutrients for living organisms because it is a fundamental component of aminosugars, proteins and nucleic acids. Moreover, the relative N enrichment of living organisms contrasts with the scarcity of available N compounds in nature, containing terrestrial biomass and soil organic matter relatively small amounts of N ($3.5 \cdot 10^{15}$ and 95-140 $\cdot 10^{15}$ g N, respectively) (Schlesinger and Bernhardt, 2013b; Vitousek et al., 1997). The atmosphere holds the largest pool of N ($3.9 \cdot 10^{21}$ g N), most of it as N_2, but only a few microorganisms are able to break the triple bond of this molecule and convert atmospheric N_2 to reactive N (biological nitrogen fixation, BNF). For that reason N often limits the productivity of many natural ecosystems (Vitousek et al., 2002b), and humans imperil the N cycle by largely increasing the amount of reactive N entering the "internal" cycling within ecosystems. In addition, the N cycle is probably the most complex of all the major elements as N has a large number of oxidation states, there are numerous mechanisms for conversion among different N compounds and a variety of environmental transport/storage processes (Galloway et al., 2004).

1.2.1 Historical perspective and human impacts

In order to understand the current state of the N cycle, it is necessary to place it into its historical context. Both Galloway and Cowling (2002) and Galloway et al. (2004) outline the main historical events related to the N cycle based on the comprehensive revision about the history of N by Smil (2001). Nitrogen was discovered in the late 18^{th} century thanks to the work of several chemists (Scheele, Rutherford, Lavoisier and Chaptal). During the 19^{th} century, scientists learnt that N is constantly cycling between organic and inorganic compounds and that it is a common element in both animals and plants, essential for plant growth and thus a good fertilizer. However, 50 years more were needed to unravel the source of reactive N and BNF was discovered by Hellriegel and Wilfarth near the end of the 19^{th} century. Human knowledge about N was steadily growing, and so were doing the global human population and the demand for food. By that time, the scientific community realized that there was a lack of biologically available N to meet human needs for food, and a global search for natural deposits of reactive N that could be used as fertilizer began: the guano and evaporitic nitrate deposits from Pacific islands and the deserts of South America were extensively mined. More N was needed and the invention of the Haber-Bosch process – conversion of atmospheric N_2 to ammonia (NH_3) - arrived just on time, in 1913. From then on, human population started growing even faster, partly due to the increased availability of food promoted by increased N fertilisation. By the beginning of the 20^{th} century, humankind already comprehended quite well the N cycle and, unfortunately, also exerted a significant impact on it by largely raising reactive N production.

The sources of anthropogenic-borne reactive N are three: a) food production (increased cultivation of legumes and rice that promotes BNF by symbionts and cyanobacteria respectively); b) fossil fuel combustion for energy production (either N_2 or organic N are converted to NO_x, a waste product emitted to the atmosphere); and c) the already explained Haber-Bosch process. The magnitude of these impacts on the N cycle is better understood by giving some figures. Estimates for 1890 indicate that the rate of anthropogenic reactive N production was $15 \cdot 10^{12}$ g N year^{-1}, which means 5% of the total fixed N ($315 \cdot 10^{12}$ g N year^{-1}). One hundred years later, with the Haber-Bosch process already discovered and a fossil fuel based economy, the rate of anthropogenic reactive N production ($140 \cdot 10^{12}$ g N year^{-1}) increased 9-fold and reached one third of the total reactive N produced ($428 \cdot 10^{12}$ g N year^{-1}), in contrast to the 3.5-fold increase in human population (Galloway and Cowling, 2002). This unpaired growth of anthropogenic reactive N production and human population might be partly explained by the decrease in N use efficiency. For instance, in West Germany the N use efficiency for agriculture was 77% in 1951 and decreased to 38% in 1990 (van der Ploeg et al., 1997).

Although some of the human-borne alterations of the N cycle can be considered beneficial from a human point of view (a large proportion of human population is sustained by fertilized crops), there is an increasing awareness of the detrimental consequences of human impacts on the N cycle (see Galloway et al. (2004) and references therein). Currently, the large increase of reactive N incorporated into ecosystems has significantly distorted the natural N dynamics and some authors claim that the planetary boundary for the global N cycle has already been transgressed (Rockstrom et al., 2009). They warn that if the rate at which N_2 is converted to reactive N continues to increase, the resilience of important Earth subsystems will be significantly eroded. The main concern regarding anthropogenic reactive N is that its production rate largely exceeds (and it is projected to increase even more in the future) its removal rate through denitrification and NH_3 volatilisation and thus reactive N accumulates in the environment (Galloway et al., 2003). In addition, reactive N is widely dispersed and it can trigger cascade effects because the N cycle is strongly connected with other biogeochemical cycles and it influences several atmospheric, terrestrial and aquatic processes (Galloway et al., 2003). The same atom of reactive N can, in sequence, rise tropospheric O_3 levels, increase fine particulate matter, alter forest productivity, acidify surface waters, increase wetland ecosystem productivity, promote water eutrophication and increase the greenhouse potential of the atmosphere (Galloway et al., 2004).

1.2.2 Main processes of the N cycle

Soils, and especially soil microorganisms, play a crucial role in the terrestrial N cycle because most N transformations take place in the soil and are mediated by microbes. The following description of the N cycle (Fig. 1.2) starts with N_2 fixation (the main source of reactive N) and is based in some of the many detailed and comprehensive articles and book chapters written on the topic (Fageria and Baligar, 2005; Robertson and Groffman, 2015; Schlesinger and Bernhardt, 2013b; Sprent, 1987). Atmospheric N_2 is naturally fixed by lightning and then deposited on the

soil (small proportion), or mainly by the BNF carried out by some soil microorganisms. If they are free-living organisms, after dying their N will become part of the SOM. If the N_2-fixing microorganisms are symbionts, they will provide plants with inorganic N, which enters into the trophic chain. In the end, all terrestrial organisms will be transformed into SOM and consumed/degraded by a wide range of microorganisms as a source of energy, C and N. If the C/N ratio of the SOM microorganisms are feeding on is lower than their own C/N ratio (surplus of available N), most of them will release the excess as ammonium (NH_4^+) through soil organic N (SON) mineralisation or ammonification, and only a few as nitrate (NO_3^-) through heterotrophic nitrification. When the SOM has a higher C/N ratio, microorganisms are forced to scavenge additional inorganic N (usually NH_4^+) from their surroundings (NH_4^+ immobilisation). Both SON mineralisation and NH_4^+ immobilisation are ubiquitous processes as all heterotrophic soil microorganisms consume organic materials for energy and C, immobilizing and mineralizing N as well. The balance of these two processes (mineralisation-immobilisation turnover, MIT) determines the size of the inorganic N pool, which is usually very small compared to the organic N pool. If the soil pH is high, NH_4^+ can be converted into NH_3 gas and then volatilized to the atmosphere, but in general NH_4^+ is further oxidized to NO_3^- under aerobic conditions, a process called (autotrophic) nitrification that is performed by autotrophic ammonia oxidizers (NH_4^+ to NO_2^-) and autotrophic nitrite oxidizers (NO_2^- to NO_3^-). Most of the energy produced during nitrification is respired via Calvin cycle and, thus, nitrifiers are usually poor competitors for NH_4^+ compared to plant and heterotrophic microorganisms. As NH_4^+ tends to bind to soil particles but NO_3^- is easily lost from the soil by leaching or denitrification, autotrophic nitrification is an important regulator of the amount of inorganic N that stays within the soil. The NO_3^- can be denitrified and converted to N_2, which escapes to the atmosphere closing the cycle. The main denitrification pathway is carried out by heterotrophic bacteria that use NO_3^- as electron acceptor during respiration when there is a restriction in O_2 supply (following rainfall, in wetlands, in lowland rice soils or during fast mineralisation of added organic residues). There is also a non-respiratory denitrification pathway that produces mainly N_2O, but it can occur in aerobic environments and it is not coupled with bacterial growth (Robertson and Tiedje, 1987). Another alternative for NO_3^- is to be converted back to NO_2^- and NH_4^+ through dissimilatory nitrate reduction to ammonium (DNRA) (Silver et al., 2001), although this process carried out by some facultative and obligate fermentative bacteria is thought to be quantitatively less important than nitrification and denitrification. Nitrogen gases can be also produced in soils through oxidation of NH_4^+ and NO_2^- to N_2 (anaerobic ammonium oxidation, anammox) (Jetten, 2001; Mulder et al., 1995), or through chemodenitrification, an aerobic transformation of NO_2^- into N_2 or NO_x (Robertson and Groffman, 2015). However, these processes are not well understood yet and they are thought to be minor pathways in terrestrial ecosystems. Moreover, during autotrophic nitrification, NO and N_2O are often produced as by-products.

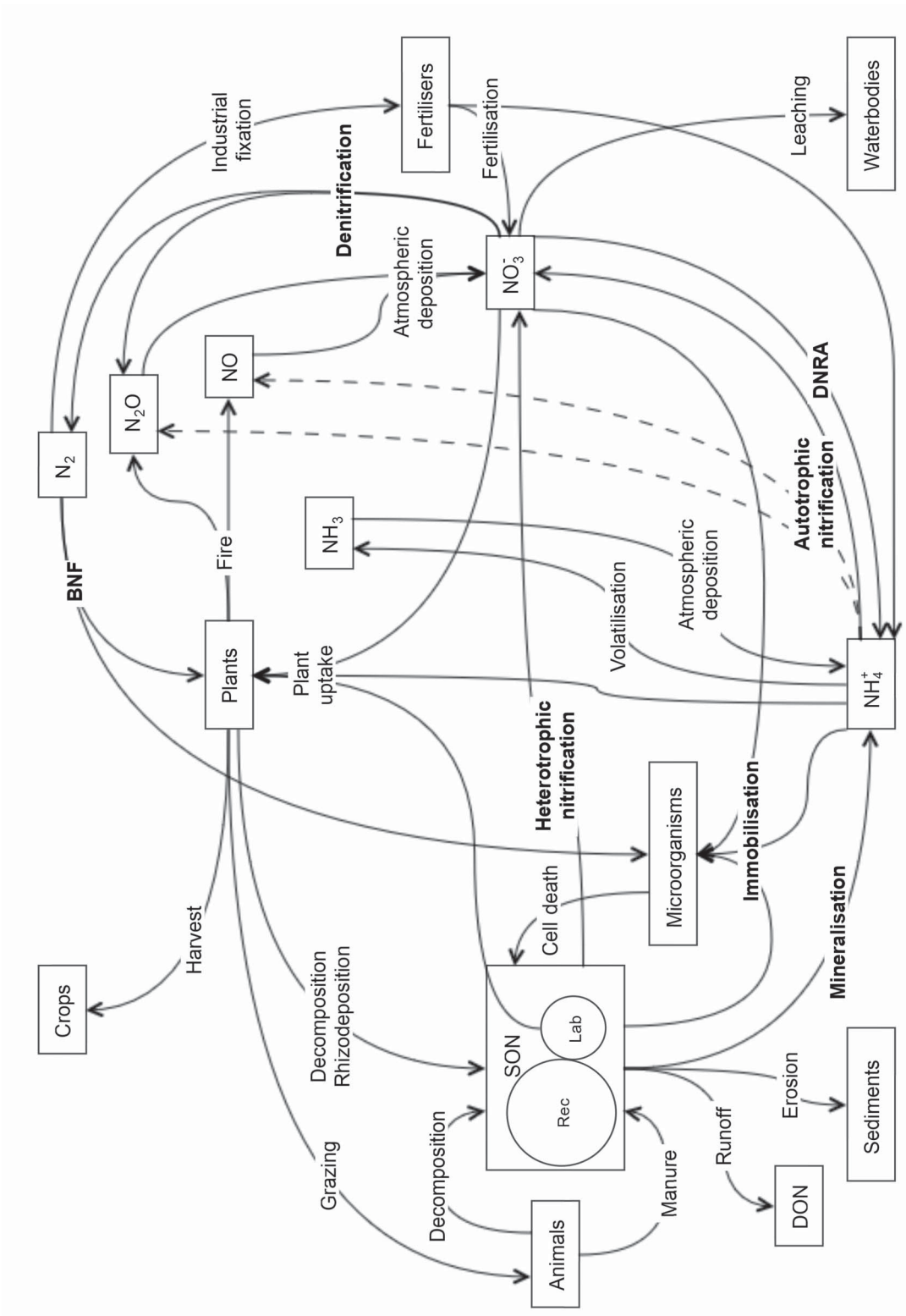

Figure 1.2: Schematic representation of the terrestrial N cycle. Processes mediated mainly or exclusively by microorganisms are highlighted in bold. SON: soil organic N; Rec: recalcitrant; Lab: labile; DON: dissolved organic N; DNRA: dissimilatory nitrate reduction to ammonium (adapted from Robertson and Groffman (2015)).

Extra supplies of either organic or inorganic N can be incorporated to the soil by fertilisation (around 170 · 10^{12} g N $year^{-1}$, see Fageria and Baligar (2005)) and deposition of inorganic N (NO_y and NH_x) from the atmosphere (103 · 10^{12} g N $year^{-1}$, see Galloway et al. (2004)). Reactive N may temporarily leave the soil system through plant uptake. Until recently, N mineralisation has been considered one of the key processes of the soil N cycle because plants were supposed to use only inorganic N and to be poor competitors for N against microorganisms, however newer conceptual models suggest a more flexible soil N cycle, mainly driven by the depolymerisation of N-containing polymers, process that varies as ecosystem N availability changes (Schimel and Bennett, 2004). The N taken up by plants might not return to the same soil system if the plants are harvested, consumed or burnt. Recovery of N in crop plants is usually around 50% of the added N as fertilizer (Fageria and Baligar, 2005), and biomass burning can return around 37 · 10^{12} g N $year^{-1}$ to the atmosphere as N_2 (Schlesinger and Bernhardt (2013b) and references therein). Soil reactive N can also leave the system through leaching and erosion, ending up in water systems and connecting the terrestrial N cycle with the aquatic N cycle. Globally, rivers carry around 60 · 10^{12} g N $year^{-1}$ from land to the sea, being anthropogenic N responsible for more than half of it. Oceans also get N through BNF and deposition, and reactive N leaves aquatic systems mainly through denitrification. Although the marine N cycle is not well understood yet, there is no doubt that it is very dynamic and it seems that the amount of reactive N in the ocean remains relatively stable over long time periods (Gruber and Galloway, 2008).

1.2.3 How to quantify gross N transformation rates

Net N mineralisation is relatively easy to measure and has been widely used as an index for plant-available N (Schimel and Bennett, 2004). Nevertheless, net N mineralisation is the outcome of counteracting gross mineralisation, gross immobilisation and nitrification taking place simultaneously, and thus quantification of all these rates separately allows a better understanding of the role of plants, microorganisms and different N pools in the N cycle (Murphy et al., 2003).

Methods to quantify gross N transformation rates in soils rely on ^{15}N labelling experiments based on the principle of ^{15}N isotope enrichment and dilution: the initially labelled pool is replenished with unlabelled material as soil N transformation processes take place and the non-labelled pools become enriched with ^{15}N as the added ^{15}N tracer is transformed (Mary et al., 1998; Stark, 2000). By measuring ^{15}N-enrichments and the change of N pool sizes over the incubation period, gross transformation rates are calculated with either analytical or numerical methods (Murphy et al., 2003). Three main assumptions must be met in order to correctly apply these ^{15}N labelling techniques: 1) microorganisms involved in the soil N cycle do not discriminate between ^{14}N and ^{15}N; 2) the applied ^{15}N is uniformly distributed throughout the soils and hence the ^{15}N-enrichment of the inorganic N pool is uniform; and 3) equilibrium between applied and indigenous N pools is achieved and thus any N transformation process would equally affect both pools (Murphy et al., 2003).

Kirkham and Bartholomew (1954) and Kirkham and Bartholomew (1955) were the first applying the ^{15}N pool dilution technique to calculate gross mineralisation and immobilisation with an analytical method. They considered two pools (mineral and organic N), added $^{15}NH_4^+$ as a tracer, monitored the NH_4^+ pool over time for isotopic excess and N content and used a set of equations to calculate gross immobilisation and gross mineralisation. These two papers set the basis for calculating N rates using the ^{15}N pool dilution technique, but some key aspects were not taken into account. First of all, they did not consider independent NH_4^+ and NO_3^- pools, necessary distinction because the two fractions are not metabolised in the same way (Mary et al., 1998). Secondly, they assumed that the organic N pool, whose size is very important for calculating the N recycling rate, was homogeneous; but subsequent studies have demonstrated that the active organic N pool (the main source for mineralisation and sink for immobilisation) is smaller than the total organic pool (see Mary et al. (1998) and references therein). No losses of N were assumed; however, small but significant losses of N often occur (volatilisation, denitrification and leaching), and thus gross N immobilisation should not be calculated considering only the mineral N balance in the soil (Mary et al., 1998). In fact, the gross immobilisation rate calculated in Kirkham and Bartholomew (1954) refers to the consumption of the inorganic N pool (NH_4^+ or NO_3^-) rather than gross immobilisation *per se* because the equation used includes all the processes removing N from the ^{15}N-labelled pool (Murphy et al., 2003). Finally, in their first paper (Kirkham and Bartholomew, 1954) no remineralisation of the newly added N was assumed, although subsequent experiments have demonstrated that remineralisation does occur (see Murphy et al. (2003) and references therein). The equations proposed in the second paper (Kirkham and Bartholomew, 1955) allowed remineralisation of the labelled ^{15}N added; nevertheless, this equation has not been widely adopted because its use is constrained to simple two-pool models (Murphy et al., 2003).

Ulterior studies have taken into account these issues and improved the analytical solutions to calculate the N fluxes (see Mary et al. (1998), Murphy et al. (2003) and references therein); nevertheless, analytical methods still have limitations. One of the main difficulties is to separately calculate the microbial immobilisation coming from NH_4^+ or NO_3^-. Some authors consider that immobilisation is the whole consumption and thus no distinction between NH_4^+ and NO_3^- immobilisation is needed. Others assume that microbial assimilation of NO_3^- is negligible when compared to assimilation of NH_4^+. Only a few studies do not make these assumptions and have tried to calculate immobilisation of NO_3^- (see Mary et al. (1998) and references therein). Another drawback of analytical solutions is that the number of parameters to be calculated is limited and more realistic models of the N cycle are needed for many soil ecosystems (Rütting and Müller, 2007). Likewise, in most equations constant or 1^{st}-order rates are assumed as they have less parameters to estimate. If mineralisation rates are low, N transformation rates can be considered linear; however, if gross mineralisation is high or the incubation period relatively long, N transformation rates become increasingly non-linear (Murphy et al., 2003). Concerning calculation errors, analytical methods calculate the rates successively and hence the error of the first estimated rate is transferred to and amplified in the

following ones (Murphy et al., 2003); in addition, no statistical information on the reliability of the estimates is provided as uncertainties for the estimated parameters are not calculated (Rütting and Müller, 2007).

Recently, different numerical solutions have been developed and they seem to be a good alternative to analytical methods as they overcome many of their limitations (Mary et al., 1998; Murphy et al., 2003; Rütting and Müller, 2007). These new ^{15}N tracing models consist on a set of differential equations solved by numerical methods and non-linear fitting routines which search for rate parameters that minimize the misfit between modelled data and a set of observed data (Müller et al., 2007; Murphy et al., 2003). In order to avoid problems of over-parameterisation, the number of fitted parameters has to be lower than the number of observed variables (Rütting and Müller, 2007). The models are designed for calculating gross N rates in the given dataset and they aim to represent the simplest description of the N transformations taking place in the analysed dataset (Myrold and Tiedje, 1986). One of the main advantages of employing numerical procedures is that transformation rates are calculated simultaneously and therefore there is no amplification of the errors towards the last calculated rates (Murphy et al., 2003). Besides, no approximation in the calculations is made as more parameters are estimated and thus not as many assumptions as in analytical solutions are needed (e.g. any kinetic order can be applied, remineralisation is allowed) (Murphy et al., 2003). Finally, the consistency of the dataset compared to the modelled system can be tested because both mineral and organic N are measured (Murphy et al., 2003).

The numerical models differ in the algorithms used to estimate the parameters and the number of them that can be estimated in each run of the model. As some algorithms enable to estimate only up to 6 parameters, the development of complex models is hampered. To overcome this limitation two strategies have been used: 1) the optimisation is carried out between two successive time points so that low N transformation rates can be ignored (Haus-Marquardt algorithm in Mary et al. (1998); or 2) the optimisation is carried out over the whole experiment but in more than one step (Simplex algorithm in Myrold and Tiedje (1986), Levenberg-Marquardt algorithm in Müller et al. (2004)). Both approaches have disadvantages because they might ignore transformation rates which are only noticeable in longer time sequences (Müller et al., 2005) or the ^{15}N data might be misinterpreted (Luxhøi et al., 2005). Moreover, due to the limited number of parameters to be estimated, N transformations are usually set to follow zero- or 1st-order kinetics instead of Michaelis-Menten kinetics, which conceptually would be better to use but requires twice as many parameters (Myrold and Tiedje, 1986). In addition, the above mentioned numerical methods use optimisation algorithms that approach local minimum in a few iterations but not inevitably global minimum (Müller et al., 2007). Consequently, the development of more complex ^{15}N-tracing models requires optimisation techniques able to estimate a large number of parameters and to identify the global minimum by an exhaustive search method that inspects the entire model space (Müller et al., 2007). The *Ntrace* model presented by Müller et al. (2007) uses a Markov chain Monte Carlo (MCMC) method in combination with the Metropolis algorithm (MA), which perform a random walk

in the model space and avoids to be trapped in local minima. This new technique allows a more complex description of the soil N processes as a large number of parameters can be unambiguously estimated (Rütting and Müller, 2007).

In the ^{15}N tracing techniques, the addition of $^{15}NH_4^+$ enables the measurement of gross mineralisation and the sum of all NH_4^+ consumption processes (NH_4^+ immobilisation, nitrification, gaseous loss and plant uptake), whereas $^{15}NO_3^-$ addition enables the estimation of gross nitrification (autotrophic plus heterotrophic nitrification) and NO_3^- consumption (NO_3^- immobilisation, gaseous loss and plant uptake) (Murphy et al., 2003). Some authors have used paired experiments (i.e. mirror labelling) in which both $^{15}NH_4NO_3$ and $NH_4{}^{15}NO_3$ are applied to different soil subsamples to simultaneously calculate mineralisation and nitrification (Mary et al., 1998; Murphy et al., 2003). However, it must be taken into account that when $^{15}NH_4NO_3$ is applied the nitrification rate becomes potential instead of actual (Murphy et al., 2003).

In order to minimize the potential errors for calculating the rates and to warrant that the underlying assumptions are met, great care in the experimental design when using ^{15}N labelling techniques should be taken (Murphy et al., 2003). Gross N transformation rates have been mostly estimated in laboratory experiments where several factors are controlled (Huygens et al., 2007; Kirkham and Bartholomew, 1954; Kirkham and Bartholomew, 1955; Luxhøi et al., 2003, 2004; Mary et al., 1998; Müller et al., 2007; Müller et al., 2004, 2006; Myrold and Tiedje, 1986; Rütting and Müller, 2007, 2008; Shindo and Nishio, 2005; Watson et al., 2000). Although understanding the processes controlling N availability in soils is most critically needed at the scale of field, farm and catchment (Murphy et al., 2003), only a few experiments have been carried out in the field due to great experimental design difficulties (Holz et al., 2016; Luxhøi et al., 2007; Recous et al., 1999; Rütting et al., 2015; Staelens et al., 2012).

The amount of ^{15}N to be added with the ^{15}N tracing technique should be carefully determined for each experiment as there is always a compromise between not increasing soil N pool sizes unrealistically and achieving enough enrichment to follow the ^{15}N pool dilution/enrichment with precision (Murphy et al., 2003). The enrichment of soil in ^{15}N can be pursued in three different ways: by applying solutions containing $^{15}NH_4^+$ or $^{15}NO_3^-$, by adding $^{15}NH_4^+$ or $^{15}NO_3^-$ salts with an inert solid carrier, and by enriching with ^{15}N the chamber atmosphere or injecting gaseous ^{15}N compounds into soil (Murphy et al., 2003). Accurate amounts of label are easier to apply with solutions than with gases and the former are also better carriers than inert solids, therefore enriched solutions have been the most used method (Murphy et al., 2003). The solutions commonly applied are $(^{15}NH_4)_2SO_4$, $K^{15}NO_3$, $^{15}NH_4NO_3$ and $NH_4{}^{15}NO_3$. The main problem with adding labelled solutions is to get a uniform distribution of ^{15}N. Mixing the soil would ensure a random distribution of transformation rates using added ^{15}N and microbial N, but the physical disturbance of the soil can potentially alter the N transformation rates (Murphy et al., 2003). To ensure an even distribution of ^{15}N avoiding further mixing, the soil depth should be kept below 2 cm and multiple drops of labelled solutions need to be applied (Murphy et al., 2003). The different injection systems normally used and their respective needle injection density and volume of delivery are reviewed in Murphy et al. (2003).

Soil heterogeneity in terms of different N transformation rates and whether native and added N pools are uniformly exploited by soil microorganisms are issues of great concern when estimating N fluxes. Watson et al. (2000) suggested an overestimation of gross N transformation rates due to preferential consumption of the applied N as a result of non-uniform mixing of the added and native N pools, opening an intense debate on this topic (Herrmann et al., 2005; Stark and Schimel, 2001; Watson et al., 2000). Finally Luxhøi et al. (2003) concluded that the results from Watson et al. (2000) could be explained by a non-homogeneous distribution of applied N while Rütting and Müller, (2007) found that if the kinetics were changed from first order to Michaelis-Menten there were no evidences of preferential use of applied NH_4^+. These results demonstrate how crucial it is for rate estimations to choose the right kinetic setting for the model (Rütting and Müller, 2007).

Although modelling major environmental issues controlled by several factors implies to schematize and simplify a highly complex reality (Bouma and McBratney, 2013), ^{15}N tracing techniques have been proven to be a powerful technique to quantify gross N fluxes in soils and they have the potential to broaden our knowledge on the soil N cycle and its linkage with the microbial function (Murphy et al., 2003). Despite the fact that this method is quickly spreading among the scientific community, Murphy et al. (2003) give warning that its use is not straight forward and incorrect application of the theory, assumptions and techniques behind it can lead to large errors in the estimation of the gross N transformation rates. They claim that the novelty of the technique has led to use it in cases in which the posed hypothesis can be tested with simpler and cheaper experiments. Moreover, they highlight that as the ratio of C mineralisation to gross N mineralisation is usually low, ^{15}N tracing techniques might measure the microbial cycling of small pools of highly labile N-rich compounds rather than the overall breakdown of SOM and growth of microbial biomass. In other words, the method might give us a proxy for microbial cellular processes rather than SOM processes (Fierer et al. (2001) in Schimel and Bennett (2004)).

1.3 Fires

"Fire is a force that shapes nature through overwhelming power, a force we cannot tame and with which we ultimately have to learn to live if we are finally to settle into the country." (William L. Baker, 2009)

1.3.1 Historical context

Earth is an intrinsically flammable planet because it has plenty of fuel (C rich vegetation), oxidizing agent (atmospheric O_2) and widespread sources of ignition (lightning and volcanoes) (Bowman et al., 2009). Fires appeared soon after the establishment of terrestrial plants, which provided oxygen and fuel (Pausas and Keeley, 2009), and as combustion needs certain atmospheric O_2 concentrations, fire activity and atmospheric O_2 levels have always been

correlated (Scott and Glasspool, 2006). Fires have affected more land area than any other natural disturbance and they recurrently occur in tropical, subtropical, temperate and boreal forests, savannahs and cultivated lands all around the world (Levine, 1991). Both burning and the resulting vegetation changes have important effects on biogeochemical cycles, climate patterns, evolutionary traits of many organisms and plant community structure and distribution, as well as on many ecosystem services (Bowman et al., 2009; Lavorel et al., 2007; Pausas and Keeley, 2009). Pausas and Keeley (2009) review the history of fires and show evidences of their role in the origins of plant adaptations and in the global distribution of ecosystems.

Although fire is a natural phenomenon in most terrestrial ecosystems, nowadays most wildfires are caused by humans, either directly through accidents, negligence, arson and side effects of human structures, or indirectly by making ecosystems vulnerable to fire (Blaud et al., 2016). Fire has been used by humans for multiple purposes: tool for hunting, land conversion (forest clearing and maintaining grasslands), pest and weed control, crop management, fuel hazard control, etc. (Lavorel et al., 2007). Nonetheless, our mastery of fire management is far from being perfect (Bowman et al., 2009), and the increasing human use of fire results in a shift of natural processes that threatens sustainability of some ecosystems (Pausas and Keeley, 2009). Caldararo (2002) analyses the relationship between forest fires and human activities, and the numerous suggested theories to explain forest changes since the late Pleistocene. After a thorough review of the literature, he concludes that current intense forest fires are a direct consequence of the increased dominance of humans, who have caused a significant reduction of herbivores and a progressively fire-adapted ecology. In fact, other authors claim that the effects of fire are to some extent analogous to those of herbivory (Bond and Keeley, 2005).

During the 20$^{\text{th}}$ century, fire regimes in temperate latitudes have changed drastically due to shifts in ecosystem characteristics and land use (Pausas and Keeley, 2009). In some parts of Europe, including the Mediterranean regions, industrialisation caused a generalized population movement from rural to industrial areas with the subsequent abandonment of farms and the reduction in livestock grazing pressure (without replacement by natural grazers), facts that led to the build-up of large and continuous fuel beds that are prone to burn (Pausas and Keeley, 2009). Moreover, during the last decades large areas have been covered by plantations of fire-prone species (e.g. eucalyptus and pine) allowing fires to spread further than they would in the native landscape (Blaud et al., 2016). Consequently, in temperate latitudes, where natural fires are possible but not as common as nowadays, the increasing number of wildfires seems to be correlated with human-driven land use changes (Pausas et al. (2008) and references therein). Nonetheless, it is still under debate whether humans or climate are more important in determining current fire patterns (Bowman et al., 2009). It is widely recognized that fire regimes and impacts depend on the interactions among climate, vegetation structure and land use, and thus fire ecology is potentially highly sensitive to global change (Bento-Gonçalves et al., 2012; Bowman et al., 2009; Lavorel et al., 2007).

1.3.2 Definitions and classifications

Wildfire, forest fire and bushfire are all terms used across the world to describe unplanned vegetation fires, whereas prescribed fire refers to those used for rural and forest management (Bento-Gonçalves et al., 2012). In general, prescribed fires aim to reduce fuel levels and to facilitate germination and growth of the desired plant species (Certini, 2005). They tend to have a lower intensity than wildfires and their impacts on ecosystems are usually less pronounced, but they have been very useful for fire research. Nonetheless their use is controversial: although some studies show evidence of their role in avoiding large wildfires by reducing fuel load, prescribed fires are also strongly criticised because they affect ecosystems to some extent and because they might even trigger wildfires (Bento-Gonçalves et al., 2012; Caldararo, 2002).

The terminology used for describing fires has been lately up for debate (Bento-Gonçalves et al., 2012). Keeley (2009) tries to untangle the terms fire intensity and fire severity and presents a simple chart relating these terms with ecosystem responses (Fig. 1.3). Fire **intensity** refers to the physical combustion process of energy release from organic matter, whereas **fire severity** (or sometimes **burnt severity**) refers to how fire intensity affects ecosystems and it usually describes the loss or decomposition of aboveground and belowground organic matter. **Ecosystem responses** refer to the processes that are affected by fire intensity, for example erosion, vegetation regeneration, faunal recolonization or restoration of community structure. However, fire severity is not the only factor determining ecosystem responses to fire; other variables such as fire type (ground, surface, and crown), temporal nature (rate of spread, seasonality, and frequency) or spatial pattern (size and patchiness) might be involved in the wide range of effects fires have on ecosystems (Bento-Gonçalves et al., 2012; Bowman et al., 2009; Neary et al., 2008). **Fire regime** refers to the general features of fires occurring within a particular vegetation type or ecosystem across long successional time frames (usually centuries) (Neary et al., 2008). Fire regime classifications can be based on fire characteristics (and they use a combination of the factors mentioned before) or on fire effects (Bento-Gonçalves et al., 2012; Brown and Smith, 2000).

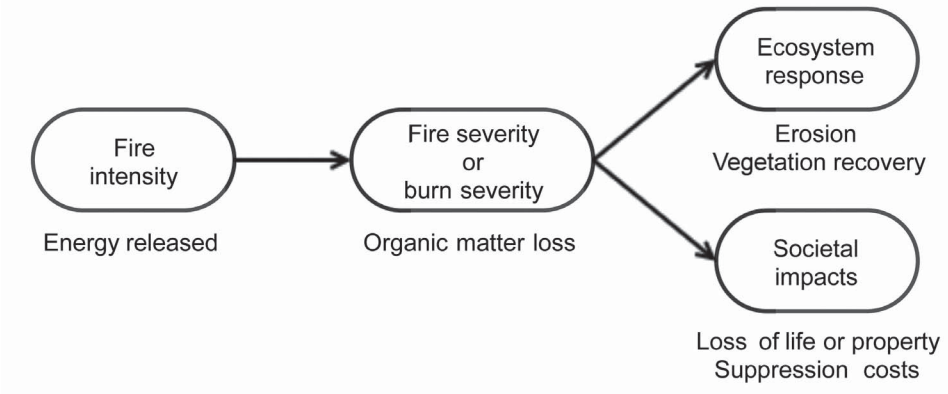

Figure 1.3: Schematic representation showing the relationship between different important terms in fire research (adapted from Keeley (2009)).

Fires can be classified according to several criteria and there is no agreement on which classification is more appropriated to predict the wide range of environmental damage caused by fires. Forest fires are usually divided into three types: ground, surface and crown (or canopy) (Shakesby and Doerr, 2006). In the US, the classification used by the Forest Service of the Department of Agriculture is based on fire regimes and defines four types: 1) understory fires; 2) stand-replacement fires; 3) mixed severity fires; and 4) nonfire (Brown and Smith, 2000; Neary et al., 2008). Vega et al. (2013a) suggest a fire severity classification with five levels based on visual indicators (Table 1.2). In Galicia, these burnt severity levels match well with changes in soil chemical and microbial properties immediately after fire and are very useful for designing emergency post-fire rehabilitation treatments (Vega et al., 2013b). As this thesis deals with fire impacts on soil properties and the efficiency of post-fire rehabilitation treatments in Galician soils, I use this classification to characterize the fires under study.

Table 1.2: Soil burn severity (SBS) levels (including an unburnt state) based on immediate post-fire visual characteristics of soil and duff (from Vega et al. (2013b)).

SBS levels	Forest floor (Oi+Oe+Oa)	Mineral soil (Ah horizon)
0	No evidence of fire.	No evidence of fire.
1	Oa layer (lower duff) partially or totally intact.	Undisturbed.
2	Oa layer totally charred and covering mineral soil. There may be ash.	Undisturbed.
3	Forest floor completely consumed (bare soil). There may be ash.	Undisturbed. Soil structure unaffected. SOM not consumed. Surface fine roots not burned.
4	Forest floor completely consumed (bare soil). There is no charred residue. Thick layer of ash.	Soil structure affected. SOM consumed in the upper layer. Surface soil colour altered (grey). Surface fine roots burned.
5	Forest floor completely consumed (bare soil). There is no charred residue.	Soil structure affected. SOM consumed in the upper layer. Surface soil colour altered (reddish). Surface fine roots burned.

1.3.3 Effects

Fires have a wide range of impacts on ecosystem functioning (Bowman et al., 2009), and understanding these impacts is paramount for post-fire rehabilitation. "Fire's Effects on Ecosystems" by DeBano et al. (1998) provides information of fire effects on ecosystem resources with a special focus on soil and water, and aims to be helpful for planning and implementing fire management activities. Similarly, the "Rainbow Series", consisting of six review publications, provides information and examples of fire effects on air (Sandberg et al., 2002), soil and water (Neary et al., 2008), fauna (Smith, 2000), flora (Brown and Smith, 2000) and cultural resources

(Ryan et al., 2012) to advance understanding of basic concepts regarding fire effects in the United States and Canada. Moreover, in the last decades fires began to be considered in documents about global environmental issues as important drivers of land degradation and their economic costs are becoming to be assessed (Blaud et al., 2016; Bowman et al., 2009; FAO and ITPS, 2015; Nkonya, 2016).

1.3.3.1 *Effects on air*

Fires are a major contributor of trace gases and aerosol species in the atmosphere. Although the main gas produced by fires is CO_2, incomplete combustion of organic matter results in emission of other gases such as CO, CH_4, other hydrocarbons, N_2O and NO_x, and aerosols (Crutzen and Andreae, 1990), being the amount, rate and nature of these substances dependant on the type of fuel, fire behaviour, fire duration and weather conditions (Sandberg et al., 2002). Estimates of fire derived emissions have large uncertainties (Alves et al., 2011), and many researchers claim that it would be very useful to obtain regional emission databases reflecting the distinct burning conditions and the associated levels of emitted gases and aerosols (see Alves et al. (2011) and references therein). The European Forest Fire Information System (EFFIS) has recently developed a beta application of a Global Wildfire Information System that maps, among other parameters, fire emissions of different gases (Joint Research Centre, 2016). Fire emissions have impacts on visibility, atmospheric chemistry, biogeochemical cycles and climate (Alves et al., 2011). Biomass burning releases CO_2, CH_4 and N_2O, three powerful greenhouse gases (Karhu et al., 2015); N_2O is also involved in the destruction of the stratospheric ozone layer (Ravishankara et al., 2009); emissions of CO and CH_4 alter the atmospheric oxidation efficiency (Crutzen and Andreae, 1990); and NO_x and hydrocarbon emissions cause an increase in tropospheric ozone (Thompson et al., 2001). Aerosols are involved in reduced visibility after fires, can negatively affect human health and have highly uncertain impacts on climate forcing (Spracklen et al., 2007).

Nonetheless, emissions from burnt ecosystems due to altered soil properties in the longer term have not been so thoroughly studied. For example, increased post-fire mineral N concentrations could enhance N emissions, but data from burnt sites points to both positive and negative effects on the microbial pathways leading to N_2O and NO_x production (Anderson and Poth, 1998; Dannenmann et al., 2011; Fierro and Castaldi, 2011; Inclán et al., 2012; Karhu et al., 2015). Medium to long term post-fire conditions may also alter the soil-atmosphere CH_4 balance. Methanotrophic bacteria living in well drained and aerobic soils oxidize CH_4 for obtaining energy, but fires, which usually lead to increased soil NH_4^+ concentrations, might reduce methanotrophic activity because NH_3 can act as a competitive substrate for methane monooxygenase (see Inclán et al. (2012) and references therein).

1.3.3.2 *Effects on water*

Fires greatly affect the hydrologic cycle and the suppression activities implemented or the post-fire precipitation regime can exacerbate these impacts. Neary et al. (2008) thoroughly describes how the different water storage components and processes are affected by fires of varying severity. In most cases, the destruction of the vegetation and changes in important soil properties lead to an altered water balance in the burnt catchment area. The removal of the plant canopy results in less evapotranspiration and a pronounced decrease in the rate of interception of post-fire precipitation and thus throughfall (water dripping from the remaining plants) and stem flow (water flowing down from the remaining stems) tend to increase. Consequently, more water reaches the soil, but the infiltration capacity of burnt soils is often reduced due to the removal of vegetation and litter, two important protective layers, and to the important alterations on SOM and soil structure. The loss of SOM causes an increase in bulk density and reduces soil porosity, and raindrop impacts produce compaction and sealing of surface soil pores. Moreover, some soils can develop water repellency after fire (see also section "1.3.3.5. Effects on soils"), a phenomenon that can further reduce the infiltration capacity of the soil because rainfall water can only infiltrate down to the water repellent layer and thus this soil layer can be easily eroded and overland flow is often increased.

All these processes taken together usually result in increased overland flow and streamflow, which are often responsible of enhanced erosion rates and altered water quality, respectively. Increased post-fire streamflow can result in substantial impacts on several physical, chemical, and biological properties of water in streams, rivers, and wetlands, being the most severe the physical impacts dealing with the sediments and ashes deposited into streams.

1.3.3.3 *Effects on fauna*

Fire direct effects on fauna (injury, mortality, immigration or emigration) are highly dependent on the fire regime and are usually of less importance than those derived by the habitat changes caused by fires, i.e., the extent of structural change in vegetation is the main factor determining longer-term fire effects on above-ground faunal communities (Smith, 2000). According with this author, altered post-fire nutrient availability can favour herbivore populations and landscape dramatic changes have an influence on raptors and preys as the latter usually lose hiding coverage and are more exposed. Animal responses to fire are therefore heterogeneous, increasing the population of some species and decreasing in others.

The impact of fire on soil biodiversity depends on the fire regime and the resulting heat flux transferred to the soil. Soil properties will determine how deep in the soil profile the heat flux reaches - large fuel loads close to the soil combined with low soil moisture contents result in strong heat fluxes that travel deep into the soil - and usually organic soil layers and the organisms living in them are the most vulnerable to fire (Blaud et al., 2016).

1.3.3.4 *Effects on vegetation*

As vegetation is the main fuel of wildfires, plant communities usually experience the most visually apparent effects of burning (Couto-Vázquez, 2011). In fact, many fire classifications are based on the damage suffered by plant communities. The wide range of fire impacts on vegetation are determined by the fire regime, and the subsequent plant recovery also depends on the characteristics of the affected plant species and on post-fire weather conditions (Quintana et al., 2004). According to post-fire strategies of vegetation recovery, plants can be classified in: a) obligate resprouters, which lack a fire-resistant seedbank; b) obligate seeders, which only rely on germination to regenerate in post-fire conditions; c) facultative seeders, which are able to resprout and to germinate after fire; and d) postfire colonizers, which recruit seeds from unburnt patches or from outside the burnt area (Pausas and Keeley, 2014). Fire regime and post-fire weather conditions not only determine certain temperature and moisture conditions, critical parameters for germination and resprouting, but also influence erosion rates, which can also impact vegetation recovery (Pausas, 1999). In moist and fertile environments, vegetation recovery after fires is very fast and resprouting confers a competitive advantage by recapturing space previously occupied by the mature plant (Pausas and Keeley, 2014), being obligate seeders often displaced in these ecosystems when recurrent fires take place (Couto-Vázquez, 2011). Nonetheless, germination of obligate seeders is usually stimulated by the heat of the fire or by other fire products such as smoke or charred wood (see Pausas et al. (2008) and references therein).

1.3.3.5 *Effects on soils*

Although the most visible fire effects are noticed on vegetation, burning also causes profound impacts on soil physical, chemical and biological properties. Research on fire effects on soils has grown in the last decades and there are several recent comprehensive reviews on the topic (Bento-Gonçalves et al., 2012; Certini, 2005; Neary et al., 2008). The main fire impacts on soils, whose magnitude and duration largely depend on fire severity, frequency and post-fire climatic conditions, include soil structure breakdown, reduction in water holding capacity, development of water repellency, changes in nutrient pools and cycling rates, element losses through volatilisation, leaching and erosion, reduction, alteration or loss of SOM, loss of microbial species and alteration of population dynamics and reduction or loss of invertebrates and plant roots (Neary et al., 2008). From a broader perspective, fire impacts on soils can affect site productivity, sustainability, biological diversity, and watershed hydrologic response (Neary et al., 2008). Post-fire soil erosion due to the removal of the protective vegetative cover and to altered soil infiltration capacity is one of the most serious fire outcomes (Blaud et al., 2016; Neary et al., 2008). Although wildfires are responsible of the most serious impacts on soils, prescribed fires can also cause important problems (Gómez-Rey et al., 2013b; Neary et al., 2008).

Around 10 to 15% of the energy released as heat by combustion of aboveground fuels is transferred to the soil by radiation and then throughout it by other heat transfer processes, such as convection, vaporisation, condensation (dry soils) or conduction (wet soils) (Neary et al., 2008). Heat transfer and depth of soil heating are important parameters for quantifying the extent of soil damage and are determined by fire characteristics (especially fuel load and duration of the fire) and soil properties (especially amount of SOM and moisture content) (Certini, 2005; Couto-Vázquez, 2011; Neary et al., 2008). Except for underground fires (e.g. peatlands) the greatest increase in temperature occurs at the soil surface and, as soils are in general poor heat conductors (especially dry soils), the temperature decreases sharply with soil depth (on average no more than 150 ℃ at 5 cm and no heating below 20-30 cm) (Certini, 2005; DeBano, 2000).

The magnitude and duration of fire impacts are not the same for the different soil properties as they have different threshold temperatures - the temperature value over which nutrients are volatilized or irreversible damage occurs to a certain soil property - (Neary et al., 2008). According to these temperature thresholds, soil properties have been classified into three groups (Neary et al., 2008): 1) relatively insensitive soil properties not affected up to 450 ℃ (clays, cations and Mn); 2) moderately sensitive soil properties altered at temperatures between 100 and 400 ℃ (S, SOM and related properties); and 3) sensitive soil properties affected at less than 100 ℃ (living soil microorganisms, plant roots, seeds and many of the biologically mediated nutrient cycles).

1.3.3.5.1 *Physical and chemical soil properties*

Perhaps the most visible effect of fire on soils is its colour change due to the deposition of grey or black ash or charred materials (Certini, 2005) and to SOM consumption that results in a greyish or reddish soil surface (Vega et al., 2013b). The temperature regime of the soil might be altered by colour changes which modify the albedo of the soil (Certini, 2005).

Soil pH increases after burning due to organic acid denaturation and to the accumulation of ashes, which are highly alkaline (Couto-Vázquez, 2011). The decrease of the cation exchange capacity reported after fires is a direct consequence of SOM combustion and also influences pH increases as SOM holds large amounts of cations (Certini, 2005). Altered soil pH can have important consequences on nutrient availability for plants. Most elements are more soluble or available in acidic soils, and extreme acidic soils can have very high concentrations of Al, Fe and Mn that might be toxic for plant growth. Phosphorus behaves slightly different: its highest availability is around pH 6.5, forming insoluble compounds with Al and Fe at lower pH and with Ca at higher pH.

The mineral soil component is usually not altered by fire because disruption of most minerals needs temperatures higher than 500 ℃ (Certini, 2005). Soil structure, greatly determined by soil aggregates, can be seriously affected by burning, depending the magnitude of the impacts on soil heating and the type of aggregates. Destruction of soil aggregates due to burning causes increased bulk density, decreased water holding capacity and the subsequent increase in erosion

risk (Certini, 2005). Whereas clay aggregates can remain unaltered up to 500 ℃, organic matter aggregates are usually affected at lower temperatures (see Couto-Vázquez (2011). Nonetheless stability of organic matter aggregates can be increased after low or moderate fires due to the formation of an hydrophobic film on their external surface (Certini, 2005). Hydrophobic compounds originate a water-repellent layer of variable thickness and spatial continuity on the soil surface or a few centimetres below that decreases soil permeability and promotes post-fire soil erosion in steep areas (DeBano, 2000). Soil water repellency is mainly determined by soil heating, but quantity and quality of SOM, soil water content and the soil-plant system as a whole also influence this phenomenon (see DeBano (2000) and references therein).

1.3.3.5.2 *Soil organic matter (SOM)*

Soil organic matter is especially sensitive to soil heating (low temperature threshold) and it lays on the uppermost soil horizons where soil heating is greater. As SOM is formed by a wide range of substances, the different SOM fractions are variously affected by heating; and the overall extent of soil heating determines the magnitude of fire effects on both SOM quantity and quality (see Neary et al., (2008) and references therein).

Loss of SOM is perhaps one of the most dramatic impact fires have on the soil system, as SOM is particularly important for biological activity, nutrient supply, cation exchange capacity, soil structure and water retention (Certini, 2005; Neary et al., 2008). Although the amount of SOM decreases immediately after the fire, in the longer-term it usually exceeds pre-fire levels due to the high net primary productivity of secondary ecological successions (Certini, 2005). The quality of SOM is also greatly affected by fires. Selective burning of fresh residues (leaves, twigs) and formation of aromatic and highly polymerised (humic-like) compounds results in an increase of recalcitrant SOM fractions compared to the more labile ones (Castro et al., 2006; Certini, 2005; Fernández et al., 2004). This shift in the proportion of labile-recalcitrant SOM has important consequences on post-fire SOM decomposition and associated processes. Decomposition usually increases during fires, although research on post-fire SOM dynamics has shown either increases and decreases of decomposition (see Neary et al. (2008) and references therein). It seems that fire severity, frequency and pre-fire soil characteristics (soil structure and moisture content) greatly determine SOM decomposition.

1.3.3.5.3 *Nutrients and trace elements*

During burning, plant biomass is combusted and the essential nutrients and trace elements forming part of plant tissues are volatilized or transformed into ash or charred material. This relocation of substances often results in increased concentrations of these elements in the soil that may last for a few months or for years, depending on how fast they are lost from the soil or taken up by plants (Neary et al., 2008). Element losses from the burnt ecosystem can be of great magnitude and have an important impact on biogeochemical cycles and ecosystem

primary production. Post fire nutrient losses are conditioned by their solubility (Certini, 2005) and by the erosion rate, which is highly dependent on the percentage of bare-ground areas and the post-fire weather pattern (Thomas et al., 1999).

Fire effects on the N cycle can be summarized as follows: removal of organic and inorganic N through volatilisation, redistribution of the remaining soil organic N (increase of recalcitrant forms and decrease of the most labile ones), conversion of organic N into NH_4^+ (combustion) and later into NO_3^- (nitrification), losses through leaching and erosion and a marked alteration of both quantity and specific composition of microbial communities (Castro et al., 2006; Certini, 2005; Neary et al., 2008; Prieto-Fernández et al., 2004).

The importance of fire-derived N losses on primary production will depend on the proportion of lost N in each affected ecosystem, being crucial in those N-limited (Neary et al., 2008). Most N losses during fires are a result of N volatilisation, process that increases with temperature (from 25% of total N at 200 ℃ to 100% at 500 ℃) and mainly produces N_2 (Neary et al., 2008). Nevertheless, post-fire N losses through leaching, erosion and altered microbial processes should not be disregarded (see also sections "1.3.3.1. Effects on air" and "1.3.3.2. Effects on water"). At first glance, fire-borne N losses seem puzzling: total N decreases due to combustion of organic matter but available N usually increases and so does plant growth (Neary et al., 2008). But this increase in fertility is usually short-lived and in the longer term the generalized reduction of total N might compromise ecosystem production (Castro et al., 2006; Couto-Vázquez et al., 2011; Prieto-Fernández et al., 1993). Modern approaches quantifying gross N rates instead of the size of different N pools and net transformation rates will provide a more comprehensive understanding of the effect of fires on the N cycle. However, little research on gross N transformation rates in burnt soils has been carried out (especially immediately after the fire), and most of the studies have used analytical methods instead of numerical models despite the already mentioned advantages of the latter (Gómez-Rey and González-Prieto, 2013) (see section "1.2.3. How to quantify gross N transformation rates").

The P cycle is also strongly affected by burning. Although P volatilisation is smaller than for N during fires, P is lost from the system faster than supplied from mineral weathering (DeBano et al., 1998). Organic P in soils is mineralized to orthophosphate, the only plant available form, resulting in a transient increase in P availability also supported by increased pH, but this short-term increase might be followed by long-term losses that can reduce ecosystem productivity (see Cade-Menun et al. (2000) and references therein).

Basic cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+), usually non limiting in most ecosystems but essential macronutrients for plant growth, experience a significant increased availability following fire. Losses through volatilisation are very low due to the high temperature thresholds of these cations, and as plant material contains large amounts of them, so does the ash deposited on the soil after plant biomass burning (Neary et al., 2008). Monovalent cations (Na^+ and K^+) are more easily mobilized (as chlorides and carbonates for example), whereas divalent cations (Ca^{2+} and Mg^{2+}) are less mobile and usually present as oxides and carbonates (Soto and Díaz-Fierros,

1993). The transient increase in base cations concentrations plays a key role in post-fire changes of base saturation and soil pH (DeBano et al., 1998).

Fire effects on soil micronutrients and trace elements (Al, Cu, Fe, Mn, Mo, Zn) have not been so thoroughly studied, although they are essential for plant growth and post-fire changes in their availability could lead to deficiencies or toxicity effects on plants (García-Marco and González-Prieto, 2008; Gómez-Rey and González-Prieto, 2014). Burning usually results in transient increases in soil concentrations of most micronutrients and trace elements, but the scarce available data is often contradictory because of the differences among the studies in terms of fire characteristics, climate conditions, vegetation cover, soil type and sampling design (soil/ash/sediment samples, time after the fire, fraction of the elements measured) (Brye et al., 2002; Close et al., 2011; García-Marco and González-Prieto, 2008; Gómez-Rey et al., 2013a; González-Parra et al., 1996; Pereira et al., 2011; Pivello et al., 2010; Ponder et al., 2009; Stankov-Jovanovic et al., 2011). Conversely to what it has been reported for macronutrients, sediments collected from burnt areas are enriched in some micronutrients and trace elements compared with ashes, most probably due to a preferential transport of fine particles and organic matter to which these elements are usually bound (Gómez-Rey et al., 2013b; Gómez-Rey et al., 2014). These enriched sediments can affect water quality if they reach the surrounding aquatic systems, or soil quality where they are deposited if soil contamination thresholds are surpassed (Gómez-Rey et al., 2014).

1.3.3.5.4 *Soil microorganisms*

Soil heating is generally lethal for soil microorganisms, and thus immediately after the fire the microbial community structure is greatly altered and soil microbial biomass tends to decrease substantially or even undergo complete sterilisation (Acea and Carballas, 1996; Barreiro, 2016; Certini, 2005; Díaz-Raviña et al., 1992; Díaz-Raviña et al., 1996). Fires cause a wide range of impacts on soil microbial communities due to their different sensitivity to heat and altered soil properties, their wide range of survival strategies and the appearance of new ecological niches (Barreiro, 2016). For instance, increased temperature and pH have an important effect on the microbial community structure by affecting the fungi to bacteria ratio. Bacteria are in general more resistant to heating than fungi (Vázquez et al., 1993), and high soil pH favours bacterial over fungal growth (Rousk et al., 2009).

In general, despite the sharp decrease in soil microbial biomass after burning, the activity of C and N mineralizing microorganisms is increased in the short-term (Díaz-Raviña et al., 1996) as the surviving communities occupy the new niches and quickly mineralize the more labile SOM fractions produced after fire. In the longer term, after exhaustion of the labile SOM, the mineralisation rates decrease and it can take several years until pre-fire levels are reached again, depending on how fast vegetation establishes in the area again and provides new inputs of labile organic matter (Barreiro, 2016).

1.3.3.5.5 *Erosion*

Soil erosion occurs naturally in most ecosystems and at different rates depending on geology, topography, vegetation and climate (Neary et al., 2008). However, nowadays soil erosion has become a worldwide problem as more than 75 x 10^{15} g of fertile soil are lost every year, a rate that is 10 to 20-fold higher than the estimated for natural soil formation (Blaud et al., 2016). Ecosystem disturbances, such as overgrazing, timber harvesting, inadequate agricultural practices, building of infrastructures and fires are the main drivers of these unnaturally high sediment yields. Increased soil erosion has important and long-lasting consequences in ecosystem functioning as it reduces soil depth, removes large amounts of nutrients and organic matter from the soil, reducing its fertility and affecting water quality in the water bodies where the eroded material is deposited.

Apart from changes in vegetation, soil erosion is the most visible and dramatic impact of fires (Blaud et al., 2016; Neary et al., 2008). Following fire, the significant removal of the plant cover and the litter layer, as well as the altered soil structure and water repellency, greatly modify water infiltration patterns and trigger post-fire erosion (Certini, 2005; Robichaud et al., 2010). Although fire-related erosion rates are highly variable and depend on several factors (topography, geology, climate, remaining plant cover, soil properties...), in some regions post-fire sediment losses account for more than 60% of the total landscape sediment production (Neary et al., 2008). Post-fire rainfall patterns greatly determine the extent and magnitude of the erosion events. Intense and usually short rainfalls produce high sediment yields (Robichaud et al., 2010), especially if the affected area is steep (Neary et al., 2008). Post-fire erosion can be briefly mitigated by the ash layer, which absorbs rainfall and results in less runoff than in areas with little or no ash cover (Robichaud et al., 2010). In fact, the amount of bare soil not covered by vegetation, litter or ash at first stages is positively correlated with post-fire erosion rates and thus, if natural mulch (i.e.: conifer needle cast) remains on the soil, or vegetation establishes again on the affected area, soil erosion rates decrease (Robichaud et al., 2010). Therefore, the highest sediment yields are usually reported during the first year after the fire and they decline in subsequent years at varying rates depending on fire severity and the speed of vegetation recovery (Neary et al., 2008).

1.4 Fire management

"I wonder if our fire training had so strongly overemphasized fire as "an enemy" that we were immune to the long-lasting adverse impacts or resource damage caused during some fire suppression activities. Were we so engrained with controlling the "fire against time" instead of "managing it with time" that we had completely overlooked our agency's motto of "caring for the land"? Suppression of a wildfire does not give us license to overlook this basic goal of land ethics and prudent land stewardship." (F. Mohr, 1992)

1.4.1 Fire policies

Since the 1990s, an increasing public and political awareness of fires as a global environmental issue has contributed to improve fire management policies and several international forums have been created to promote the dialogue between the scientific, technical and policy-making communities (Global Fire Monitoring Center, 2012). In 1998, following the recommendations of the FAO and the Second International Wildland Fire Conference (Vancouver, Canada, 1996), the Global Fire Monitoring Center (GFMC) was created to further international cooperation in fire management by monitoring and providing global fire related information, and to support countries in fire management related issues directly or through the assistance of international organisations (Fire Ecology Research Group, 2016). Since 2000, the GFMC cooperates with the Wildland Fire Advisory Group (WFAG) of the UN International Strategy for Disaster Reduction (UNISDR), an interagency and inter-sectoral forum whose aim is to serve as an advisory body to the UN system (UNISDR Wildland Fire Advisory Group and Global Wildland Fire Network, 2000). In 2001, the Global Wildland Fire Network (GWFN) was established as a set of Regional Wildland Fire Networks that included existing formal or informal structures and initiatives, or new ones in those regions where no such previous networks existed (Global Wildland Fire Network, 2016). Through periodical international and regional Wildland Fire Conferences and Summits, the Regional Wildland Fire Networks have been consolidated and promoted, and the GFMC is mandated to serve as convener and secretariat of the GWFN and WFAG. Concurrently, the Expert Consultation on Global Forest Resources Assessment, held in Finland during June 1996, recommended FAO to provide annual statistics/estimates for each country on the number of forest fires and the area burned over the period. The FAO recognized that current data on fires is still incomplete and thus it is difficult to assess the annual degradation of forests caused by wildfires. The Forest Resources Assessment 2000 process (FRA 2000) provided an opportunity to define the global effects of fires on forests and to develop a system for collecting meaningful fire data for developing countries (FAO, 2016b). Forest fire management is also within the agenda of the *Silva Mediterranea*, a FAO statutory body in which Mediterranean member countries and involved FAO Regional Forestry Commissions meet, share experiences and establish cooperative programmes (Committee on Mediterranean Forestry Questions, 2016e).

The European Union, aware of the serious impacts fires have on the environment, recognizes that prevention at European level is one of the most efficient ways to face these threats. Several working groups and commissions have been working on the topic (i.e.: Commission's Expert Group on Forest Fires since 1998) and the legislation on protecting the EU's forests against fire has improved substantially (European Commission, 2016). The European Forest Fire Information System (EFFIS), operational since 2000, aims to provide EU assessments of the full fire cycle, supplying information of the pre-fire conditions and assessing post-fire damages (Joint Research Centre, 2016). In addition, an agreement with FAO *Silva Mediterranea* was reached to extend the system to all non-EU Mediterranean countries.

Spain, as a member of both the UN and the EU, participates in many of the fire management initiatives explained before. Although each Spanish region has its own legislation on fire management and is in charge of fire prevention and fire extinction within its boundaries, the Spanish Ministry of Agriculture and Environment coordinates fire management efforts, compiles fire data and supports affected regions in fire extinction when necessary (Ministerio de Agricultura y Pesca, Alimentación y Medio Ambiente, 2016). In Galicia, fire management is regulated by the prevention and defence plan against forest fires elaborated annually (PLADIGA) (Consellería do Medio Rural, 2016c). The main aims of this plan are: 1) to organize prevention, detection, extinction and research of forest fires; 2) to establish fire risk periods according to different local parameters; 3) to reduce the ecological, economic and social consequences of fires; and 4) to plan future actions.

1.4.2 Wildfire suppression

Currently, most fires are caused by humans, and most times humans do also extinguish the fire, although in some cases fire suppression activities might result in significant environmental damage and even surpass the effects of the fire itself (Backer et al., 2004). In their review about the impacts of fire suppression activities, Backer et al. (2004) remark that until the 1980s, fire suppression activities did not take into account their potential adverse impacts on natural resources, but lately fire suppression policies have evolved and they now aim to minimize suppression costs and impacts to natural resources. Table 1.3 gathers most impacts derived from fire suppression activities, which can be briefly summarized as increased air pollution and soil compaction due to the use of heavy vehicles for fire suppression activities, and damage to fauna and flora, soil and water pollution, soil compaction and increased erosion rates as a result of construction of fire lines, temporary roads and helicopter pads.

A very common practice in countries with a high fire incidence is the aerial or terrestrial application of fire fighting chemicals (FFCs) mixed with the water in order to improve suppression efficiency. In the last decades, the use of FFCs has increased substantially, reaching in Spain 300 Mg year^{-1} (Luna et al., 2007). There are three main types of fire fighting chemicals (adapted from Backer et al. (2004)):

1.4.2.1 *Fire suppressant foams*

These chemicals, which inhibit water evaporation and dissolve the waxy coating of alive plants, are very useful in improving water effectiveness and thus reducing the amount of water needed to control the fire (Couto-Vázquez, 2011). They can be surfactant (detergent-based) foams, aqueous film-forming foams, foam stabilizers, inhibiting agents or solvents. The most widely commercialized fire suppressant foams are Ansul Silv-Ex, Angus ForExpan S, Fire Quench, 3M Firebreak and, in Spain, Auxquímia RFC-88 (Couto-Vázquez, 2011). Although these chemicals can have deletereous impacts on the environment, few research has been conducted on the topic (Adams and Simmons, 1999; Larson et al., 1999; McDonald et al., 1996; Moody and Field, 2000). Furthermore, available information is usually biased as it focus on damage to aquatic systems and overlooks impacts on soils and vegetation.

1.4.2.2 *Acrylic-based synthetic polymers (Firesorb)*

This relatively new fire fighting chemical increases water viscosity turning it into a gel and improving its efficiency in extinguishing the fire. Besides, it might improve soil structure and increase infiltration rates (Basanta et al., 2002).

1.4.2.3 *Fire retardant chemicals*

They are mainly composed of N and P and they inhibit combustion even when water is completely evaporated, lasting their effect until they are removed from the area by water or wind (Couto-Vázquez, 2011). Among fire retardants, the most commonly used are Phos-Chek D75-F, Phos-Chek D75-R and Fire-Trol GTS-R, although in Spain it is the ammonium polyphosphate FR Cross (Couto-Vázquez, 2011). Due to the low inherent toxicity of their basic components (often used as fertilizers), some years ago it was assumed that their effects on water quality, vegetation and animals should be small and short-lived (Handleman, 1971). Nonetheless, nowadays more studies point to the role of fire retardants on eutrophication of water bodies (Freedman, 1995), direct toxicity to aquatic flora and fauna (Gaikowski et al., 1996; McDonald et al., 1996; McDonald et al., 1997) and effects on terrestrial vegetation (Bell et al., 2005; Bradstock et al., 1987; Couto-Vázquez et al., 2011; Cruz et al., 2005; Larson and Newton, 1996; Larson et al., 1999; Larson and Duncan, 1982; Luna et al., 2007; Song et al., 2014).

Although studies on the effectiveness of different FFCs have grown since their implementation, research on their effects on ecosystems has not been as thorough. Giménez et al. (2004) reviewed the different aspects that influence the final effectiveness of FFCs and the environmental impacts on streams, aquatic organisms, vegetation and humans. Surprisingly, FFC effects on soils did not deserve scientific attention until recently (Couto-Vázquez et al., 2011; Couto-Vázquez and

González-Prieto, 2006; García-Marco and González-Prieto, 2008) and there is still a lack of information about their long-term effects. Moreover, to understand the impacts of FFCs on ecosystems as a whole is a complex task as FFCs impacts largely depend on the type and dose of the applied FFC, how often it is applied on a certain area and the resilience of the ecosystem to both burning and FFC addition. Since FFC use might compromise soil fertility and hence reestablishment of plant communities (including areas with high environmental values and endangered plant species), it is crucial to assess the long-term consequences that FFC addition has on the soil-plant system under different scenarios.

Table 1.3: Impacts associated with fire suppression activities (from Backer et al. (2004)).

Element affected	Impact	Potential sources
Earth	soil compaction	fire camps fire lines helibases incident command posts road construction
	erosion	fire lines road construction
	non-native species	fire camps fire lines helibases incident command posts rehabilitation activities (seed mixes,straw-bale check dams)
	litter and waste	fire camps fire lines extinguished fuses, line explosives, and aerial ignition devices rehabilitation activities
	reduction of habitat	contour-felled logs (rehabilitation activities) snag removal (mop-up activities)
	soil contamination	fuel spilage
Air	air pollution	fossil fuel emissions:aircraft, vehicles, machinery
	noise pollution	acrial support
	visual pollution	increase of air traffic
Water	sedimentation	contour-felled logs and channelization fire camps fire lines road construction
	disturbance	amphibious aircraft removal of water for suppression activities (heli-buckets, pumping)
	fish mortality	fire retardant
	eutrophication	fertilizer use with rehabilitation activities fire retardant
	pollution	fire camps fire retardant fuel spillage rehabilitation activities (introduction of synthetic materials)

1.4.3 Post-fire treatments

The increasing number of wildfires as well as the growing awareness of their impacts on both natural ecosystems and human infrastructures has resulted in a more widespread use of post-fire treatments (see Robichaud et al. (2010) and references therein). The US is the leading country concerning research and implementation of post-fire treatments, and already in the late 20th century the Burn Area Emergency Rehabilitation (BAER) was founded as a formal authority for post-fire rehabilitation activities (Robichaud et al., 2000). The BAER assessment team defines emergency in the context of post-fire treatments as any post-fire scenario that threatens life, safety and property or cause unacceptable degradation of natural and cultural resources (Napper, 2006). These treatments are divided into three types according to their specific objectives and timing of the processes (Robichaud et al., 2010). Emergency stabilisation treatments are conducted during the first year after burning to stabilize the burnt area, whereas rehabilitation and restoration activities are conducted in the longer term and their aim is to mitigate land damage that is unlikely to recover on its own. This thesis will focus on post-fire emergency stabilisation treatments and, in particular, on straw mulching.

It is paramount to assess the effectiveness and practicality of post-fire emergency stabilisation treatments, although this type of studies is scarce because direct measurements of erosion require a rapid response research protocol, are time consuming, labour-intensive and generally expensive (Robichaud, 2005; Robichaud et al., 2010). Concurrently, a thorough assessment of burnt areas in terms of fire severity, climate, topography, soil and watershed status, and the potential risk of damage for different resources should also be done in order to decide whether post-fire emergency stabilisation treatments should be applied and, in that case, which treatment is the most appropriate (Napper, 2006). Both burnt area assessment and emergency stabilisation treatment implementation should be done as soon as possible so treatments are applied before the first damaging rain event occurs (Robichaud et al., 2000). Deciding which treatment to use, as well as when and where it should be used, involves weighting the costs and effectiveness of a certain treatment against the potential damage from unmitigated erosion (Robichaud, 2005). The suitability of using onsite materials as mulch should be also considered, as it reduces the cost and time for transporting mulch materials to the burnt areas (Robichaud et al., 2010). Fortunately, the number of research syntheses and reference catalogues about wildfire effects on soil, hydrology, erosion and post-fire emergency stabilisation treatment effectiveness is constantly growing (Bautista et al., 2009; Beyers, 2009; Moody et al., 2013; Napper, 2006; Parson et al., 2010; Peppin et al., 2010; Robichaud, 2005; Robichaud and Ashmun, 2013; Robichaud et al., 2010; Robichaud et al., 2013a; Robichaud et al., 2013b; Shakesby et al., 2016). Moreover, new tools such as prediction models, equipment and methods for field measurements, databases of past-practice and spreadsheets for calculating resource valuation and cost-benefit analysis, are now available for land managers to facilitate burnt area assessment and treatment decisions (Robichaud and Ashmun, 2013).

Emergency stabilisation treatments are divided into several subclasses: land treatments, channel treatments, road and trail treatments and protection and safety treatments (Napper, 2006). According to BAER, land treatments aim to reduce fire impacts and foster ecosystem recovery by providing soil cover, trapping sediments, improving infiltration, preventing expansion of unwanted species and reducing erosion, sedimentation and water repellency (Napper, 2006). The main types of these land treatments are summarized in Table 1.4.

Mulch refers to the cover placed over the soil to reduce the effects of rain impact and overland flow and to keep the soil in place; and, as ground cover is immediately increased, mulching is very effective during the critical first post-fire year when erosion is likely to be high (Bautista et al., 2009). Mulching is often used in combination with seeding of grass species because it improves moisture retention and thus the seeding success is increased (Robichaud et al., 2010). Mulching is most probably among the most effective post-fire stabilisation treatments, but factors such as site conditions, material used and application rate and technique greatly influence treatment effectiveness (Bautista et al., 2009). The mulches can be divided into two groups according to the application technique: wet mulches (hydromulch) prepared by mixing water with the mulch material to obtain a slurry, and dry mulches that are applied without water (Robichaud et al., 2010). Both wet and dry mulches can be applied from helicopters (helimulching) or from the ground by hand or with blowers, and the most common mulch materials are straw, jute, wood excelsior, wood chips or wood shreds (Bautista et al., 2009). Between 60% and 80% of ground cover is needed to reduce hillslope erosion, being the percentage of bare soil covered more important than the mulch material used; however, the longevity of the mulch material, its thickness and its propensity to stay in place are also important factors constraining mulching effectiveness (see Robichaud et al. (2010) and references therein). Due to the high costs of mulch application, its use is only recommended in burnt areas with a high soil erosion potential and where important downstream values are at risk (Bautista et al., 2009; Robichaud et al., 2010).

Agricultural straw from wheat, rice and barley are probably the most widely used materials for post-fire mulching (Bautista et al., 2009). They began to be used in the 1980s, but its application significantly spread since 2000 when the number of large fires in the US increased substantially (Robichaud et al., 2010). The straw cover effectively reduces erosion rates because it provides immediate ground cover and protects bare soil from raindrop impact and overland flow (Robichaud et al., 2010; Robichaud et al., 2013a). Moreover, straw mulch increases soil infiltration capacity, moisture content and aggregate size and reduces surface compaction and temperature, creating a more favourable microclimate for seed germination (Bautista et al., 2009; Robichaud et al., 2010). Straw mulching is most effective when an even application of consistent thickness is achieved, and usual straw rates range between 2.2 and 2.4 x 10^6 g ha^{-1}, which corresponds to about 70% of ground cover (Bautista et al., 2009). The main disadvantage of straw mulching is that seeds from non-native species may be introduced with the applied straw and compete with the re-growing native vegetation (Bautista et al., 2009; Robichaud et al., 2010). Although "weed-free" straw is now available, its use is not always feasible depending on the location of the burnt site and the amount of straw needed (Robichaud et al., 2010).

Table 1.4: Land treatment types and brief description (information extracted from Bautista et al. (2009) and Napper (2006)).

Land treatment	**Description**
Hydromulch (aerial and ground)	All-inclusive term that includes fibres mulches and soil stabilizers (tackifiers, polymers, and seeds) that, when mixed with water and applied to the soil surface, form a matrix that helps reduce erosion and fosters plant growth. They can be applied from aircrafts or from the road using truck-mounted applicators.
Dry mulch	Provides immediate ground cover and protection to soils from erosion. Most common mulch materials are straw, jute, wood excelsior, wood chips or wood shreds. Dry mulch is applied with helicopters (helimulching) to treat large areas, or by hand for smaller treatment sites.
Slash spreading	Involves felling, lopping, and scattering submerchantable trees and brush to provide soil cover with available onsite materials.
Erosion control mats	Provide soil stability to sites until vegetation can establish. They are either synthetic or organic and temporary or permanent. Organic mats are biodegradable and made from a variety of materials including coconut, wood excelsior (aspen), or straw. Material is contained in lightweight netting that lasts from several months to several years.
Log erosion barriers	Include contour felled logs, log terraces, or terracettes placed in a shallow trench on the contour. They trap sediment if laid in a bricklayer pattern on the hillslope. The potential volume of sediment stored is dependent on slope, size, and length of the felled trees, and proper implementation.
Fibre rolls or wattles	Prefabricated rolls manufactured from rice straw and wrapped in ultraviolet degradable plastic or jute netting. They are used in high-burn severity areas where soil erosion and water quality deterioration are at risk and log erosion barriers are not practical.
Silt fences	Geotextile fabric installed with wooden posts or metal T-posts that traps sediment. They are often used in areas with high values at risk where other treatments, such as log erosion barriers or fibre rolls may be ineffective.
Soil scarification	Raking of the soil on the contour to reduce overland flow and erosion by increasing infiltration and creating surface roughness, break hydrophobic layers and prepare the seedbed to foster seed germination and growth.
Seeding	Seed can be applied with aircrafts (large treatment units) or with belly grinders (smaller treatment units). Seeding minimizes soil and wind erosion by providing vegetative cover and it may prevent the introduction and increase of noxious and invasive plants. As it is ineffective the first year, it is included with other treatments, such as straw mulching, hydromulching, or soil scarifying.
Invasive plants	Includes chemical, biological, hand, mechanical, or prevention-seeding to treat invasive plants.
Hazardous-material stabilization	Include stabilizing or removing toxic materials created or destabilized by the fire.
Heritage-site stabilization	Protects the qualifying site characteristics from exposure by erosion, overland runoff, sun baking, and mechanical disturbance without displacing or damaging the remains.

Section 2

Context of this thesis

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Most of the Iberian Peninsula belongs to the Mediterranean biome (Mediterranean ecoregion), whereas the northern part is included in the temperate biome (Eurosiberian ecoregion). According to recent publications, Galicia belongs to the temperate biome (absence of summer droughts), although the close contact of the Southeast of Galicia with the Mediterranean biome (more than two months of summer droughts) determines a bioclimatic gradient in the region (Rodríguez Guitián and Ramil-Rego, 2007). Similarly, Galicia is included in the Eurosiberian ecoregion, although the flora of some valleys in the southeast area has a strong Mediterranean influence (Rodríguez Guitián and Ramil-Rego, 2008).

The historical evolution of Galician landscape has been thoroughly explained in several publications (Carballas, 2003; Consellería do Medio Rural, 2016a). Briefly, we can say that the climax deciduous broad-leaved forests were cleared out since the mid-Holocene (Kaal et al., 2011) for several purposes (timber production, charcoal production and conversion to pastures) and subsequently shrublands expanded (mainly *Ulex* spp. and *Erica* spp.). In rural areas people used these shrubs as domestic fuel and also for livestock grazing and bedding. Cattle manure mixed with the shrubs used for bedding (usually leguminous species) were highly valuable as fertilizers for croplands and thus *Ulex* spp. were extensively planted since the 18th century until the 1950s. Nonetheless, forest and shrubland harvesting practices experienced a drastic change in the second half of the 20th century due to several factors. Wood was replaced by fossil fuels and, besides, the shift from extensive livestock farming towards a more industrialized system and the incorporation and massive use of inorganic fertilizers led to a decreasing grazing pressure, a decreasing use of shrubs for livestock bedding and a change from manure to slurry production. By the second half of the 20th century, deforestation of native slow growing forests was counterbalanced by massive monospecific plantations of pines and eucalyptus (fast growing and fire-prone species), policy that was reinforced in the 1990s by the European subsidies promoting reforestation of abandoned arable land. In 50 years (1950-2000), Galicia increased its forested area from 26% to 69%, becoming one of the regions with the largest forested surface (16% of the country) (Consellería do Medio Rural, 2016a). Until the 1940s most of Galicia's land was private, followed by communal ownership and only a small percentage belonged to the State or the municipalities. However, after the Civil War, much of the communal land became property of the State and was reforested, damaging local economies as afforestation competed with extensive grazing and causing public unrest that sometimes ended up in arson. This conflict was not solved until the 1980s, when communal ownership was restored. Population-wise, Galicia's inhabitants are highly scattered across the territory (more than half of Spanish municipalities belong to Galicia) (Instituto Galego de Estatística, 2016; Instituto Nacional de Estadística, 2016). In addition, during the last decades there has been a significant population ageing and population density is decreasing in the rural areas; two common processes throughout Europe but especially dramatic in Galicia, where two out of four provinces (Lugo and Ourense) show the worst demographic indicators in the EU (Eurostat, 2016). In conclusion, all the aforementioned facts have contributed to the drastic shift in forest and shrubland use and to the increased fire incidence in the region, among the highest in Europe (Fig. 2.1).

The latest statistical report about fires in Spain provided by the Spanish Ministry of Agriculture and Environment (Cubo María et al., 2012) corresponds to the 2001-2010 period and includes a brief summary of the previous 50 years, during which the number of fires and total burnt area increased until the mid-1990s and then decreased (Fig. 2.2). A suggested explanation for the decrease in fire incidence is the increasing investment in prevention experienced since the 1990s, as well as improvements in extinction efficiency and the increasing number of punitive laws against arson (Cubo María et al., 2012). However, the graph with the number of fires and total burnt areas (Fig. 2.2) indicates that since 1990 the burnt area tends to decrease (except for 1994), but the number of fires increases until 2005. That means that prevention efforts were not as effective as suggested by public authorities and that the decrease in total burnt surface is most probably due to the increasing investment in extinction. Nonetheless, we should bear in mind that in these 50 years the means and exhaustiveness to gather fire data has evolved and the classification of fires in "fire outbreaks", "normal fires" and "large fires" according to the extent of the burnt area has been modified. Therefore, data of the whole time series should be cautiously compared.

If we focus on the 2001-2010 decade, both the number of fires and total burnt area was lower at the end of the period, although 2005 and 2006 were especially dramatic years (2005 was the year with the second highest number of fires since fire data retrieval began in 1961; Fig. 2.2). Most of the fires took place during the summer (August, followed by July and September), although there was another fire peak in March of similar magnitude to July or September. Fire causes have been classified in five groups: lightning, negligence or accident, arson, propagation of previous fires and unknown causes. Anthropogenic causes (negligence, accidents and arson together) accounted for 78% of the total number of fires (82.6% of the total burnt area); being arson the most common cause (55% of fires, 60% of burnt area). Arsonists' most common motivations are burning of agricultural residues and burning for pasture regeneration. In Spain, the most affected tree species were *Pinus pinaster*, *Pinus halepensis*, *Eucalyptus globulus* and *Quercus ilex*, because they are among the ones covering largest areas and also because they are more vulnerable to fire.

The large differences in climate, landscape and anthropogenic land use of the different Spanish regions determines the patchy distribution of fires across the country. Since long ago, Galicia has been one of the regions with highest fire incidence: between 1961 and 2011, Galicia suffered 250,000 fires that accounted for 1,850,000 ha, almost two thirds of the total area of the region. Although Galicia only accounts for 6% of Spanish surface, between 2001 and 2010 it suffered 42% of the fires and accumulated 25% of the total burnt area (Fig. 2.3). Nonetheless, the trend in Galicia for the number of fires and the annually burnt surface is similar to the general trend for Spain (Fig. 2.3). As in the rest of Spain, anthropogenic causes of fire dominate in Galicia, but arson is much more common (72% of the fires in Galicia, 55% in Spain) and negligence or accidents scarcer (8% of the fires in Galicia, 28% in Spain) (Cubo María et al., 2015). The most affected tree species were *Pinus pinaster* (occupies 15% of forested areas and burnt 54,000 ha),

Eucalyptus globulus (occupies 35% of forested areas and burnt 41,000 ha) and *Quercus robur* (occupies 20% of forested areas and burnt 5,000 ha) (Consellería do Medio Rural, 2016a).

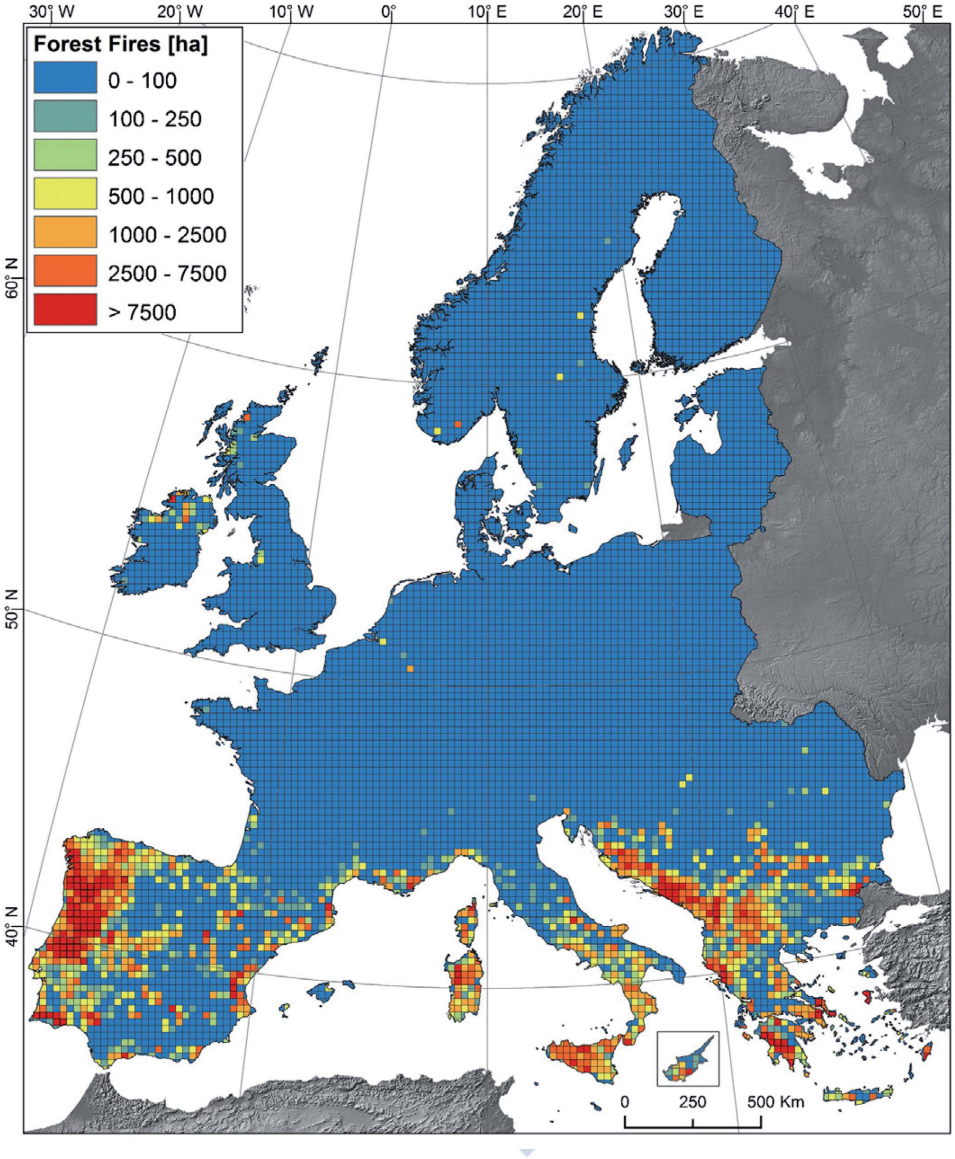

Figure 2.1: Map of forest fires reprocessed by the European Forest Fire Information System (from Borrelli et al. (2016)).

Galician landscape features such as the temperate-humid climate, the dense vegetation (shrubs and trees) and the well-developed soil organic horizons protect ecosystems against erosion. However, this scenario is reverted following fires and one of the main factors contributing to low erosion rates, the precipitation regime that favours dense vegetation and deep organic soil horizons, becomes an important threat for burnt soils in steep areas (Vega et al., 2013a). Although high precipitation rates can favour the development of a protective vegetative cover in burnt areas, the timing and intensity of the rain events might also contribute to increased erosion rates. Díaz-Fierros et al. (1987) stated that Galicia has a climate with a high potential rain aggressiveness, and such rain pattern determines the high post-fire erosion risk of the region.

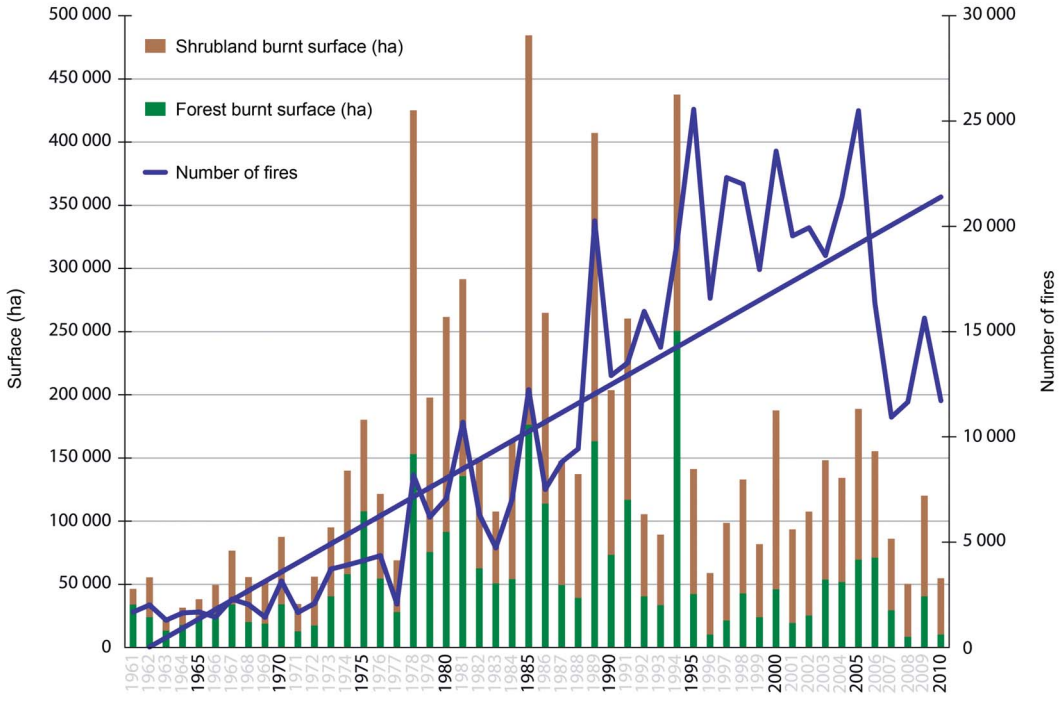

Figure 2.2: Number of fires and total burnt area per year in Spain from 1961 until 2010 (adapted from Cubo María et al. (2012)).

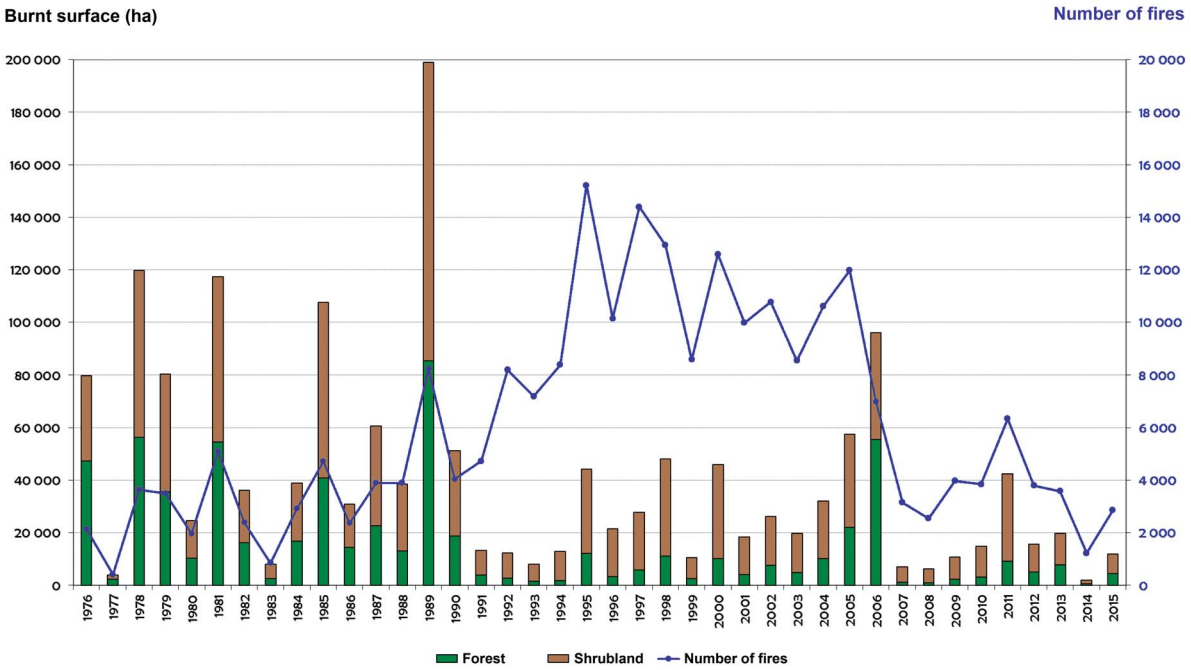

Figure 2.3: Number of fires and total burnt area per year in Galicia from 1976 until 2015 (Consellería do Medio Rural, 2016c).

Most fires in Galicia take place during the summer and intense autumn rains often take place when the vegetative cover of burnt ecosystems has not developed yet, triggering significant soil

losses through erosion. Moreover, as fire recurrence in Galicia is quite high, erosion arises as an important problem because soil loss is exacerbated in areas repeatedly affected by fires, compromising soil fertility in the long-term (Vega et al., 2013a).

Post-fire vegetation recovery in Galicia is characterized by a short lived increase (up to 2 years) in plant biodiversity due to the fast establishment of grass species from the seedbank or from nearby areas (Couto-Vázquez, 2011). Regarding shrub vegetation affected by burning, resprouting seems to be more widespread than seeding in Galician ecosystems, and obligate seeders such as some *Erica* spp. or other facultative seeders can be displaced from burnt ecosystems while *Ulex europaeus* and other strong resprouters, which moreover build extensive soil banks of pyrophyte seeds, dominate in repeatedly burnt areas (Couto-Vázquez, 2011). Both *Pinus pinaster* and *Eucalyptus globulus* are the tree species most affected by fires because they are the more abundant tree species in Galicia. Whereas *Pinus pinaster* individuals suffer more from crown fires and often recolonize burnt areas through seedlings, *Eucalyptus globulus* trees are more sensitive to fire in their trunks and quite resistant to crown fires and their preferred recolonization strategy is resprouting (Couto-Vázquez, 2011). As *Quercus robur* forests are often found in more humid areas, in general they do not burn as intensely as other species. Nonetheless, following fire they are prone to be attacked by fungi and both their seeding and resprouting abilities are hampered (Couto-Vázquez, 2011).

Proper and complete fire management policies should include fire prevention, fire suppression, burnt area assessments and post-fire treatments; however, fire management in Galicia mostly focus on wildfire suppression activities (Barreiro, 2016). Unfortunately, little resources are invested on prevention (either through education programs or through landscape maintenance) or on investigating the effects of fires and implementing post-fire treatments to rehabilitate burnt areas. In Galicia rehabilitation and restoration activities have been successfully implemented in the last decade, but knowledge and practical experience on application of post-fire emergency stabilisation treatments is much more limited (Vega et al., 2013a). The regional government did not realize how important such measures are until the catastrophic fire season in 2006, when they began to invest more resources both on research and implementation of post-fire emergency stabilisation treatments (Vega et al., 2013a). As a result, there are now a manual to quickly assess burnt severity and adequately plan post-fire stabilisation strategies (Vega et al., 2013a) and several studies that provide valuable information about the effectiveness and practicality of these treatments in different burnt areas spread across the region (Díaz-Raviña et al., 2012; Gómez-Rey et al., 2013a; Gómez-Rey et al., 2013b; Gómez-Rey et al., 2014; Gómez-Rey and González-Prieto, 2014).

Despite the fact that the most common cause of fires in Galicia is arson, education for fire prevention is not among the priorities of public authorities. In fact, the regional plan for fire prevention establishing the resources that the regional government provides local authorities only considers landscape maintenance (Consellería do Medio Rural, 2016b). This means that public authorities do not try to solve the root of the problem as no effort is made to convince people that fire is not a sustainable practice and no information of alternative and sustainable

land use practices is provided. Fortunately, there are several communal and individual initiatives working on increasing population awareness of fire outcomes and implementing sustainable land management practices that promote local economies, as well as asking for more institutional implication on the topic. Two good examples of these initiatives are the Committee to Defend Galician Forests (Comité de Defensa do Monte Galego) that claims for a new agroforestry policy to eradicate fires and the Batefogo Project (https://batefogo.wordpress.com/) that promotes fire prevention through social intervention. The scientific community working on fire effects and fire management practices is also doing an effort to inform both regional authorities and the society of their findings and to increase public awareness of fire impacts on the environment and on our society.

Section 3

Objectives and overview of the thesis

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Nowadays fires pose a serious threat for many ecosystems as they have significant ecological and economic impacts. Within Europe, fires are especially troublesome in the Mediterranean region, although in the Iberian Peninsula the highest fire incidence is usually recorded in its north-western corner, which has temperate-humid climate. Although current fire suppression strategies greatly contribute to quickly extinguish fires, they usually have high economic costs and some fire suppression activities might cause significant environmental damage, even surpassing the effects of the fire itself. Despite the potential ecological impacts of fire-fighting chemicals, in Galicia their use has greatly increased in the last decades. Deleterious effects of FFCs on aquatic organisms and water bodies are well known, whereas the impacts of these chemicals on soils and terrestrial plants have not been so thoroughly studied.

Since recently, effective post-fire rehabilitation measures to prevent erosion are being implemented in areas that have been severely affected by fires. In Galicia, straw mulching in steep burnt areas effectively reduces soil losses through erosion, although there is almost no information on the effects that straw addition can have on other important ecosystem processes such as biogeochemical cycling.

In order to effectively extinguish fires without aggravating their consequences and to protect burnt ecosystems from further degradation, it is paramount to assess when and where these measures should be applied and to optimize them in terms of resources and funds invested. Although collaboration and data sharing from different regions around the globe affected by recurrent fires is highly valuable, regional differences in terms of topography, climate, fire regime and socioeconomic factors hinder generalisation in terms of suitable fire suppression and post-fire rehabilitation plans. On this basis, the main objectives of this thesis apply to the north-western corner of the Iberian Peninsula and can be summarized as follows (see also Fig. 3.1 and Table 3.1):

- **To assess how fire and three fire-fighting chemicals (FFCs) affect the soil-plant system in the long term (10 years) (Section 4).** After a prescribed fire conducted in Tomiño (Pontevedra) in July 2003, a long-term multidisciplinary field experiment was set up to test the effects of fire and three FFCs on the soil-plant system. Five treatments (unburnt and burnt controls and burnt soils with each of the three selected FFCs) were assigned to a total of 20 plots. Within the scope of this thesis was to assess long-term fire and FFCs effects (10 years after the fire) on soil pH, soil available nutrient and trace element concentrations, as well as on coverage, height and total nutrient content of the dominant plant species.

- **To optimize the post-fire stabilisation technique based on straw mulch application, so it is economically viable, and to assess the effects of its application on soil nutrient dynamics (Section 5).** More specifically, the aim was to evaluate the effects of straw mulching on some soil and sediment properties; and to assess the efficiency of two straw mulching application strategies (narrow and wide bands along the contour lines leading to global straw doses of 800 and 1000 kg ha^{-1}, respectively)

in reducing nutrient losses in eroded sediments. In order to accomplish these objectives, after a wildfire that took place in September 2012 nearby Saviñao (Lugo), 12 experimental plots were set up within a steep and homogeneous part of the whole burnt area and the 3 treatments (burnt control plots and burnt plots with straw applied in narrow and wide bands) were applied. Soils and sediments were periodically sampled and analysed for pH, available nutrient content and total mass (only sediments).

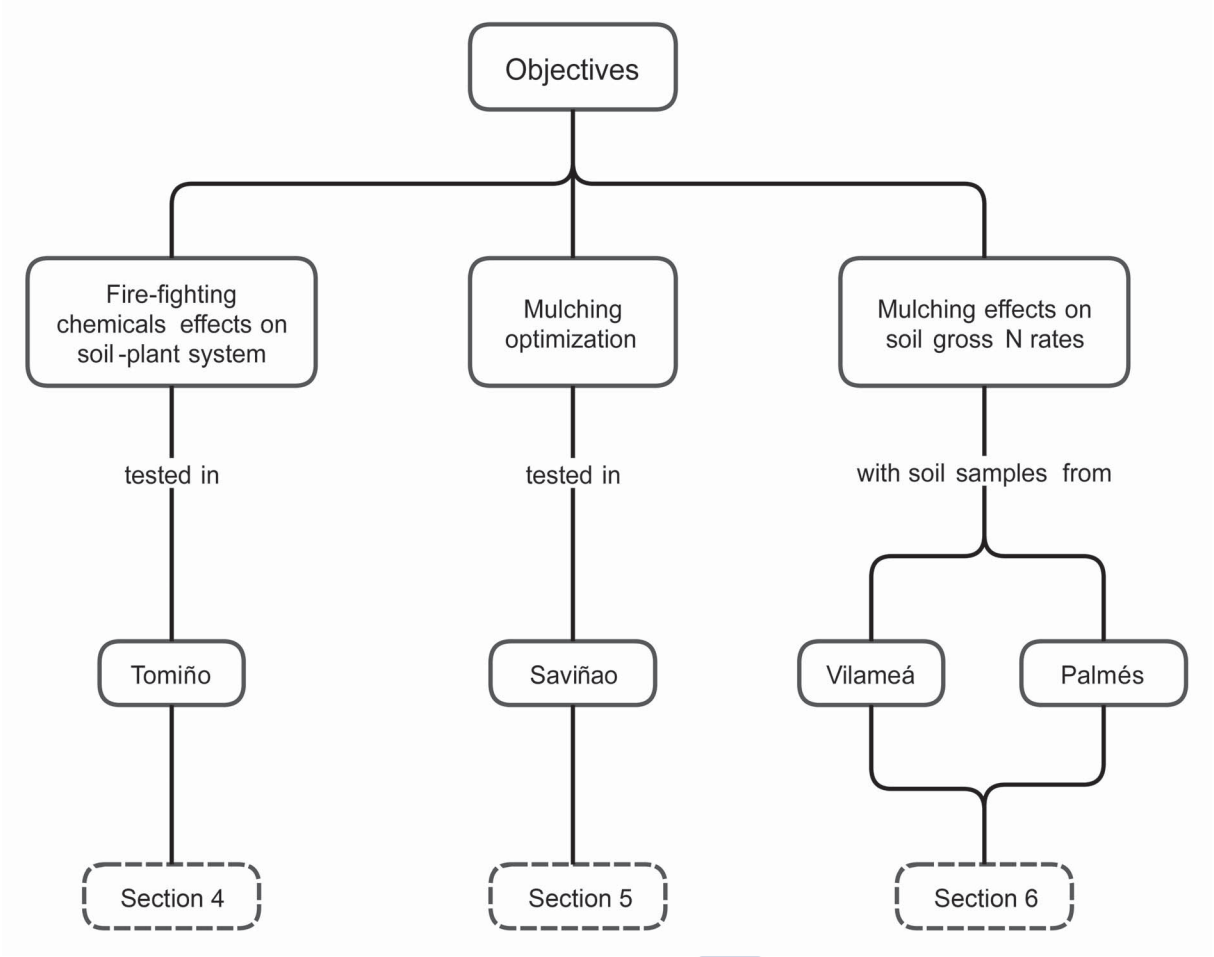

Figure 3.1: Objectives of the thesis and their relationship with the study sites and sections.

- **To evaluate the effects of fire, fire severity and straw mulching on soil gross N transformation rates (Section 6).** Among the most serious environmental consequences of fires are those related with altered soil N dynamics. Moreover, although straw mulching is highly effective in reducing soil erosion, little is known about the consequences straw addition might have on burnt soil N dynamics. Fire effects on ecosystems are usually heterogeneous and that makes research on burnt soils very challenging. Although field studies are highly valuable to integrate fire impacts on a broader perspective, the extent of fire impacts on a certain ecological process can be highly variable across the burnt area and thus laboratory experiments under controlled conditions are often necessary to understand the mechanisms behind the observed changes. Besides,

the N cycle comprises several processes mediated by a wide range of microorganisms, which might be affected directly or indirectly by fire in different ways. Therefore, it is pertinent to first develop an experimental design that allows us to unequivocally assess the effects of fire and straw addition on gross N transformation rates, and afterwards scale up this experimental design to bring together all the other variables that jointly affect the soil N cycle on a field scale. Within the scope of this thesis was to set up two ^{15}N tracing experiments in order to quantify gross N transformation rates and to assess the effects of different burning severities and straw mulching on N fluxes. The first experiment was conducted in the laboratory with highly burnt soil samples collected after a wildfire in Vilameá (Ourense) in July 2014 and from a nearby unburnt area of similar characteristics. Soils were split in three treatments (unburnt control, burnt without straw and burnt with straw) and were preincubated under optimal temperature and humidity during 3 and 6 months to accelerate the evolution of the soil-straw mixture and, therefore, to detect any possible effect of straw. Following preincubations, a ^{15}N labelling experiment was conducted and gross N rates were estimated with *Ntrace*, the most sophisticated N tracing model available nowadays. The second experiment was carried out with burnt soil (and the pertinent unburnt controls) from an area affected by a wildfire that took place in the summer 2015 in Palmés (Ourense). In this case, burnt soils were sampled from both medium and highly burnt spots according to fire severity, resulting in five treatments: unburnt control, burnt (medium severity) with and without straw, and burnt (high severity) with and without straw. Soils were also preincubated for 3 and 6 months, but outdoors so weather conditions were as close as possible to those in the field. As in the first experiment, gross N transformation rates were estimated by means of a ^{15}N labelling experiment and the subsequent modelling with *Ntrace*.

Table 3.1: Description of the study sites, the fires and the type of studies conducted.

Study site		Tomiño	Saviñao	Vilameá	Palmés
Province		Pontevedra	Lugo	Ourense	Ourense
Coordinates		42° 0′ 36″ N, 8° 46′ 49″ W $29T^{05}18^{46}50$	42° 40′ 2″ N, 7° 37′ 1″ W $29T^{06}13^{47}24$	42° 4′ 45″ N, 7° 28′ 36″ W $29T^{06}26^{46}59$	42° 21′ 4″ N, 7° 56′ 23″ W $29T^{05}87^{46}89$
Altitude (m a.s.l.)		455	530	480	420
Slope (%)		18-19	33-38	20-23	35
Bedrock		Paragneiss	Slate	Schist and quartzite	Adamellitic granite
Soil type (WRB 2014)		Dystric Leptosol	Umbric Leptosol	Dystric Leptosol	Dystric Leptosol
Vegetation		Shrubland	Shrubland	Shrubland with scattered pine trees	Pine forest (*Pinus pinaster*)
Fire	**Type**	Prescribed fire	Wildfire	Wildfire	Wildfire
	Size (ha)	0.1	85	6	230
	Date	July 2003	September 2012	August 2014	July 2015
Unburnt control		Yes	No	Yes	Yes
Type of study		Field study	Field study	Laboratory (preincubation and ^{15}N tracing experiment)	Outdoors (preincubation) + laboratory (^{15}N tracing experiment)
Sampling date(s)[a]		PF Immediately AF 1 and 3 months AF 1, 5 and 10 years AF	1, 3, 6, and 9 months AF 1 and 2 years AF	1 day AF	3 days AF
Soil preincubation		No	No	3 months (laboratory) 6 months (laboratory)	3 months (outdoors, October 2015 - February 2016) 6 months (outdoors, October 2015 – May 2016)

[a]PF pre-fire; AF: after fire

Section 4

Effects of fire and three fire-fighting chemicals on main soil properties, plant nutrient content and vegetation growth and cover after 10 years

Section 4 is based on the following paper:

Fernández-Fernández, M., Gómez-Rey, M.X., González-Prieto, S.J. (2015) Effects of fire and three fire-fighting chemicals on main soil properties, plant nutrient content and vegetation growth and cover after 10 years. *Science of The Total Environment* 515–516, 92-100.

4.1 Abstract

The study addresses a knowledge-gap in the long-term ecological consequences of fire and fire-fighting chemicals. Ten years after a prescribed fire and the application of three fire-fighting chemicals, their effects on the soil-plant system were evaluated. Five treatments were established: unburnt soils (US) and burnt soils treated with water alone (BS), foaming agent (BS+Fo), Firesorb (BS+Fi) and ammonium polyphosphate (BS+Ap). Soils (0-2 cm depth) and foliar material of shrubs (*Erica umbellata, Pterospartum tridentatum* and *Ulex micranthus*) and trees (*Pinus pinaster*) were analysed for total N, δ^{15}N, and soil-available and plant total macronutrients and trace elements. Soil pH, NH_4^+-N and NO_3^--N; pine basal diameter and height; and shrub cover and height were also measured. Compared with US plots, burnt soils had less nitrates and more Mo. Although differences were not always significant, BS+Ap had the highest levels of soil available P, Na and Al. Plants from BS+Ap plots had higher values of δ^{15}N (*P. pinaster* and *E. umbellata*), P (all species), Na (*P. tridentatum* and *U. micranthus*) and Mg (*E. umbellata* and *P. tridentatum*) than other treatments; while K in plants from BS+Ap plots was the highest among treatments for *P. pinaster* and the lowest for the shrubs. Pines in US plots were higher and wider than in burnt treatments, except for BS+Ap, where the tallest and widest trees were found, although half of them were either death (the second highest mortality after BS+Fi) or had a distorted trunk. BS+Ap was the treatment with strongest effects on plants, showing *E. umbellata* the lowest coverage and height, *P. tridentatum* the highest coverage, *U. micranthus* one of the lowest coverages and being the only treatment where *Genista triacanthos* was absent. Consequently, it is concluded that both fire and ammonium polyphosphate application had significant effects on the soil-plant system after 10 years.

4.2 Introduction

Wildfires are an important issue due to their impacts not only on the burnt ecosystems but also on the adjacent systems (agricultural, urban, transports, watersheds...) (Birot, 2009). Moreover, the time span of their effects ranges from the combustion period up to a few decades afterwards (Birot, 2009). Climate change and the shift in land use will very likely contribute to an increase in the extent and number of wildfires (Birot, 2009; Pereira et al., 2011).

The application of water added with fire-fighting chemicals (FFCs) helps to extinguish wildfires; therefore, this strategy has been widely used since the 1930s (Giménez et al., 2004). Research on FFCs has been mainly focused on their effectiveness as fire extinguishers (see Giménez et al. (2004)). As most FFCs are used in natural areas, sometimes with high wilderness or landscape values, more attention should be paid to their potential effects on the ecosystems (Adams and Simmons, 1999; Pesqueira et al., 2005). Most of the times, FFCs are applied by aircraft and it is virtually impossible to target the chemicals exclusively to the burning area. Consequently, there are three possible scenarios under realistic wildfire-fighting conditions: (1) the retardant reaches soils in the fire line and both soil and retardant are affected by the heating

and oxidation caused by the fire; (2) the retardant reaches soils in the burnt area which are still hot or warm; and (3) the retardant reaches soils close to the fire line but not affected by the fire. Most studies are focused on the last two scenarios, probably due to the problems derived from studying the narrow and very heterogeneous area of the first scenario (Couto-Vázquez et al., 2011).

In the 1980s it was already suggested that the high amounts of N and P present in many FFCs could have a fertilizing effect on plants in burnt areas (Neary and Currier, 1982). Although longer-term studies would be better to assess the consequences of FFC application on vegetation (Couto-Vázquez et al., 2011; Giménez et al., 2004), some studies already available show that some plant communities are affected in different ways by FFCs in the short-term. Larson and Duncan (1982) studied the effects of application of diammonium phosphate (DAP) as a fire retardant on burnt and unburnt grassland areas in California. They found that native legumes failed to establish on the plots treated with DAP, possibly due to the high amounts of N it released, and that treated areas doubled their biomass and were more intensively grazed by cattle than the untreated ones. Bradstock et al. (1987) found that an ammonium sulphate retardant applied on a forest of *Eucalyptus* and *Angophora* in New South Wales produced leaf (but not tree) death and varied levels of foliage damage to understorey shrubs, depending on the species and the extent of retardant coverage. Compared to untreated areas, they also found a decrease in vegetation cover for 19 of 45 species in the plots treated with the FFC. Larson and Newton (1996) conducted some experiments in North Dakota prairies with Phos-Check G75-F (an N- and P-based FFC) and the foam suppressant Silv-Ex (an N-based FFC) alone and in combination with fire. Results showed that the former increased biomass, decreased species richness, inhibited leaf production in some species and triggered dominance of the weed *Poa pratensis*; and the latter decreased species richness and increased insect herbivory. In a subsequent study with the same treatments in a North Nevada shrub steppe, Larson et al. (1999) found that although species richness was affected in the short-term by Phos-Check, after a year the larger impacts on plant communities were due to the burning rather than to any chemical treatment. Bell et al. (2005) studied the effect of Phos-Check on an Australian heathland and found that a single application did not change species composition substantially, although it caused plant death of some species and weed invasion at high concentrations of retardant. Laboratory experiments with unheated soils treated with Fire-Trol 934 (an N- and P-based FFC) showed that seed germination and seed viability of several Mediterranean species decreased when exposed to the chemical (Cruz et al., 2005; Luna et al., 2007). Recently, Song et al. (2014) found that three fire suppressant foams (Forexpan S, Phos-Chek-WD881, and Silv-ex) reduced seed germination rates in the laboratory, but did not affect seedling emergence rate of the tested species in the field.

Despite the important role soils play in terrestrial ecosystems, the effects of FFCs on soils have been scarcely studied and only in recent years (Giménez et al., 2004). In a 3-month laboratory experiment with heated and unheated soils treated with the fire retardant Firesorb (a terpolymer of acrylic acid and acrylamide), there were no major adverse effects of the retardant on the soil

microbial community, the heating itself being a greater factor affecting the microorganisms (Basanta et al., 2002; Díaz-Raviña et al., 2006). García-Villaraco et al. (2009) assessed the effects of Fire-Trol 934 during one year on burnt and unburnt Mediterranean pastures and also concluded that the application of the fire retardant caused minimal or negligible negative effects on functional diversity and total activity of soil microorganisms. Hopmans et al. (2007) applied Phos-Check to an Australian heathland and found that the addition of the retardant caused a transient change of pH (lower), and salinity and available N (both higher), although pre-treatment levels were reached again one year later. Phosphorus also increased considerably and P levels one year after Phos-Check application were still high despite evidence of P leaching into the subsoil, suggesting possible long-term impacts on growth and composition of the heathland vegetation which is very sensitive to high concentrations of P. The influence of fire, Fire-Trol 931 (an N- and P-based FFC) and pine seedlings on leachates from pots was evaluated by Koufopoulou et al. (2014), Pappa et al. (2006) and Pappa et al. (2008) in a laboratory experiment. These authors found that the FFC increased the leaching of N (substantially) and P, as well as that of Na, Fe and Si which were mobilized by the FFC-derived NH_4^+; the fertilizer effect of the FFC also favoured the growth of pines planted in the pots, where N and P leaching was consequently reduced. Therefore, the effects of N- or P-based FFCs on soil and water are cause of increasing concern and have led to the search for more environmentally friendly FFCs, as magnesium carbonates (Liodakis and Tsoukala, 2010).

Up to now, the most comprehensive field experiment on the long-term influence of FFCs on terrestrial ecosystems assessed throughout five years the effects of fire and FFCs on soils (chemical, biochemical and microbial properties) and plants (size, coverage and nutrient content of dominant species) (Barreiro et al., 2010; Couto-Vázquez et al., 2011; Couto-Vázquez and González-Prieto, 2006; García-Marco and González-Prieto, 2008). These authors set up the so-called "Tomiño experiment" in a medium size experimental area (1000 m^2) on a NW Spain shrubland, where they applied three FFCs (foaming agent RFC-88, acrylic acid-acrylamide terpolymer Firesorb and ammonium polyphosphate FR Cros 134 P) immediately after a prescribed fire. Their results showed an increase in available N and P, which was especially strong and long-lasting in the ammonium polyphosphate treatment; a factor that could delay vegetation recovery in these plots (Couto-Vázquez et al., 2011; Couto-Vázquez and González-Prieto, 2006). Five years after the fire, shrub cover and height, as well as pine size and mortality, were affected by the ammonium polyphosphate and to a lesser extent by the terpolymer (Couto-Vázquez et al., 2011). Changes in the microbial community structure were also detected five years after the prescribed fire, being more noticeable in the terpolymer and the ammonium polyphosphate plots (Barreiro et al., 2010).

These results suggest that the effects of FFCs on soils and plants can persist even after five years, making it necessary to broad the time span of the studies on this topic. Therefore, the aim of this paper (Fig. 4.1) is to extend from 5 to 10 years the "Tomiño experiment" and to analyse total N, $\delta^{15}N$ and soil-available and plant total macronutrient and trace element concentrations

on soils and foliar material of the dominant shrubs and tree species. Moreover, soil pH and inorganic forms of soil N were measured, as well as plant size and coverage.

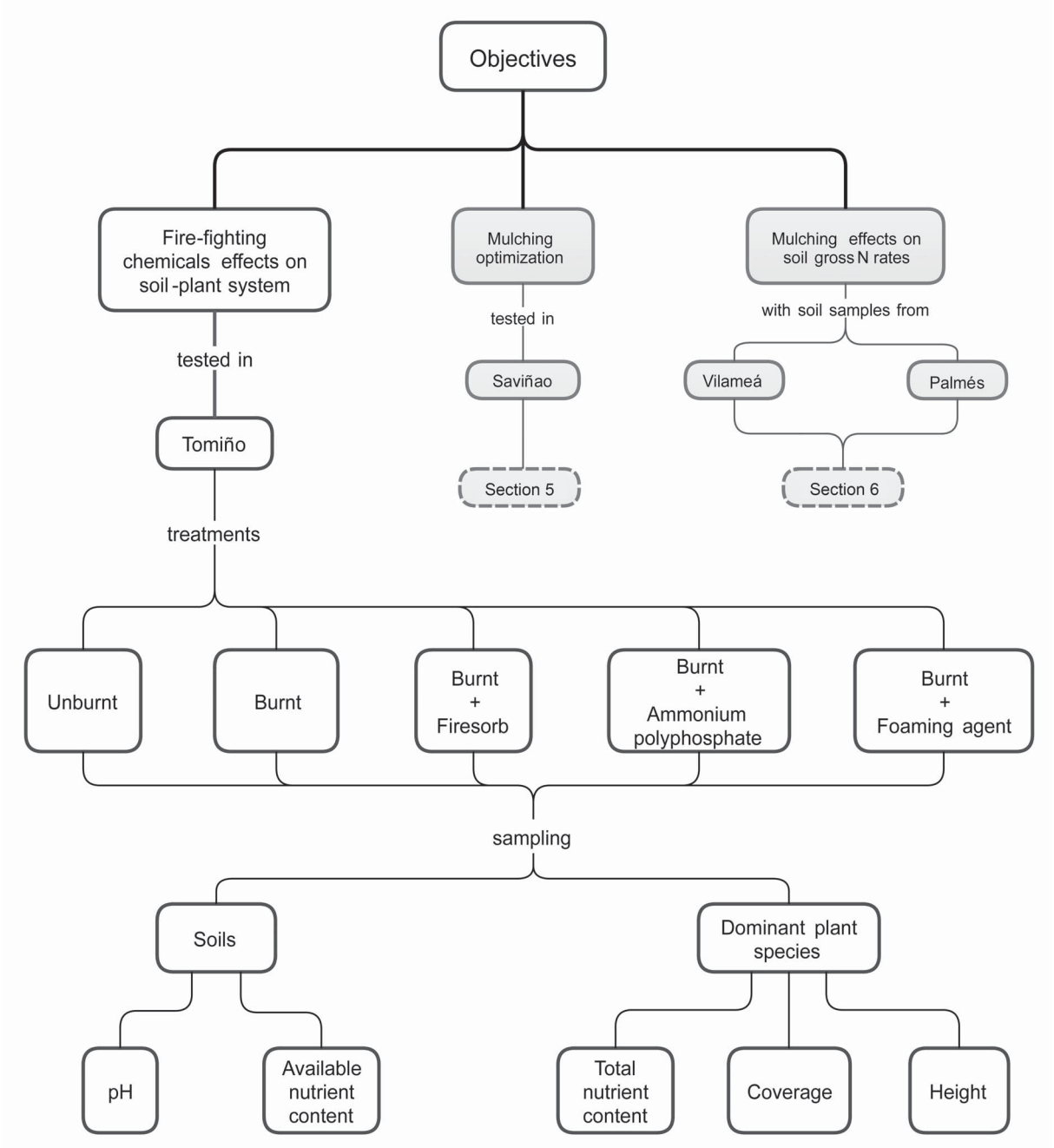

Figure 4.1: Schematic representation of the main objectives of the thesis, highlighting the specific aims, treatments and analyses of the current section.

4.3 Material and methods

4.3.1 Study area and experimental design

The experimental area, located at Alto da Pedrada (Tomiño, Galicia, NW Spain; UTM coordinates 29T $^{05}18$ – $^{46}50$; altitude of 455 m asl; Fig. 4.2), has been previously used by the authors' research team (Barreiro et al., 2010; Couto-Vázquez et al., 2011; Couto-Vázquez and González-Prieto, 2006; García-Marco and González-Prieto, 2008). The soil, developed over a parent material of paragneiss and with a slope of 18–19%, had in 2003 a vegetation cover of approximately 50-60 cm height dominated by *Pterospartum tridentatum*, *Erica umbellata* and *Ulex europaeus*, and there were also some individuals of *Ulex micranthus*, *Ulex minor* and *Erica cinerea*. In the summer of 2003, within a total surface of 40 x 25 m, five in situ treatments were established (Fig. 4.3): plots in the unburnt area (US) as a control; and plots in the burnt area that would receive 2 L m^{-2} of water alone (BS) or water with foaming agent at 1% (BS+Fo), with Firesorb at 1.5% (BS+Fi) or with ammonium polyphosphate at 20% (BS+Ap). After a prescribed fire (i.e. with the fire extinguished but with the soil still warm), burnt soil treatments were arranged in a fully randomized design with four replications per treatment and 1 m separation around each plot (4 × 4 m), whereas the four unburnt soil replicates were established along the slope and adjacent to the burnt ones (Couto-Vázquez and González-Prieto, 2006). As the area is under a high grazing pressure, the plots were fenced after the prescribed fire.

The firefighting chemicals were selected among the most widely used in countries of the Mediterranean basin: RFC-88 is a foaming agent produced by Auxquimia SA; Firesorb is a light cross-linked terpolymer of acrylic acid, acrylamide and acrylamidopropanesulfonic acid sodium salt, manufactured by Evonik Stockhausen Gmbh; and FR Cros 134 P is an ammonium polyphosphate produced by Chemische Fabrik Budenheim KG. Data on density, total nutrient concentrations and $\delta^{15}N$ of the three firefighting chemicals are available in previous papers (Couto-Vázquez and González-Prieto, 2006; García-Marco and González-Prieto, 2008).

Seven months after the prescribed fire, four 1-year old pine seedlings (supplied by a forest nursery from a genetically similar stock) were planted in each plot to follow their development and to assess how the fire and FFCs affect post-fire reforestation. Height and basal diameter of pines were measured quarterly during the first 3 years and then 4, 5 and 10 years after the prescribed fire.

4.3.2 Soil and plant sampling and processing

The soil–plant system was characterised 10 years after the fire as it was done 5 years before (i.e. 5 years postfire) (Couto-Vázquez et al., 2011). After removing the plant litter layer, soil samples were taken from the A horizon (0-2 cm depth). Five 15 x 15 cm squares, uniformly distributed within each plot, were sampled, sieved at 4 mm, mixed and thoroughly homogenised. The

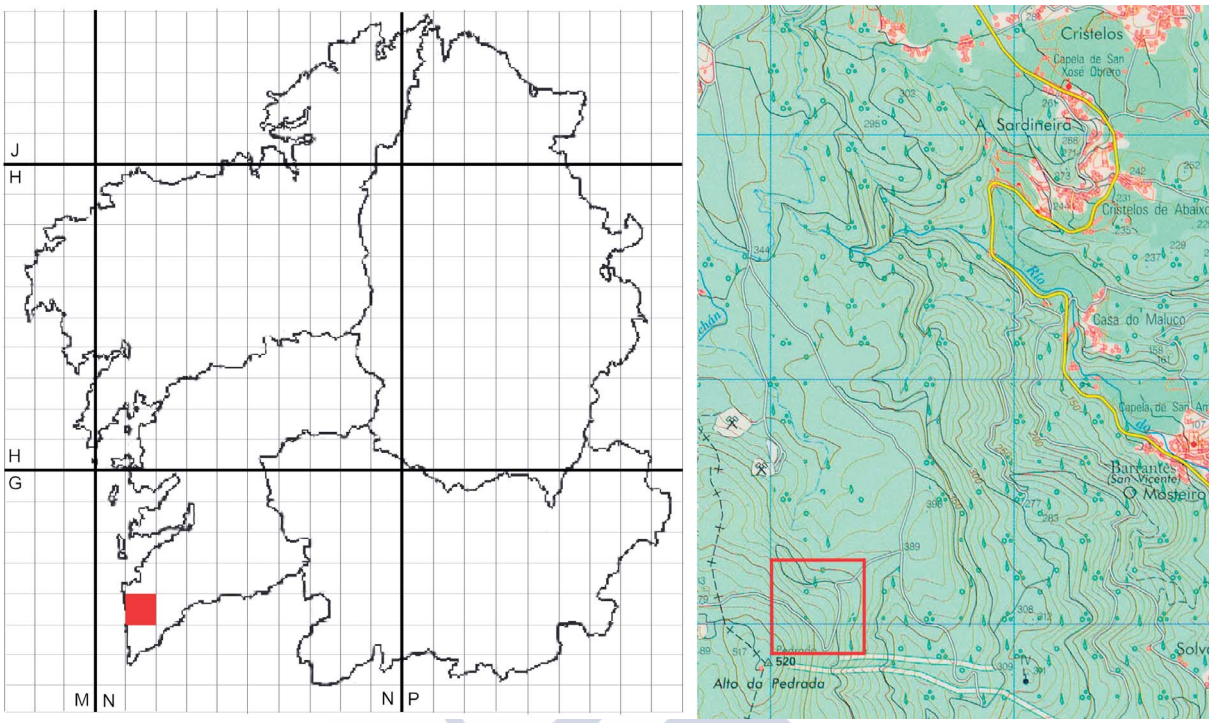

Figure 4.2: Location of the Tomiño experimental field (red square) in the 10x10 km UTM grid map of Galicia (left) and in the topographic map with 1x1 km UTM grid (right).

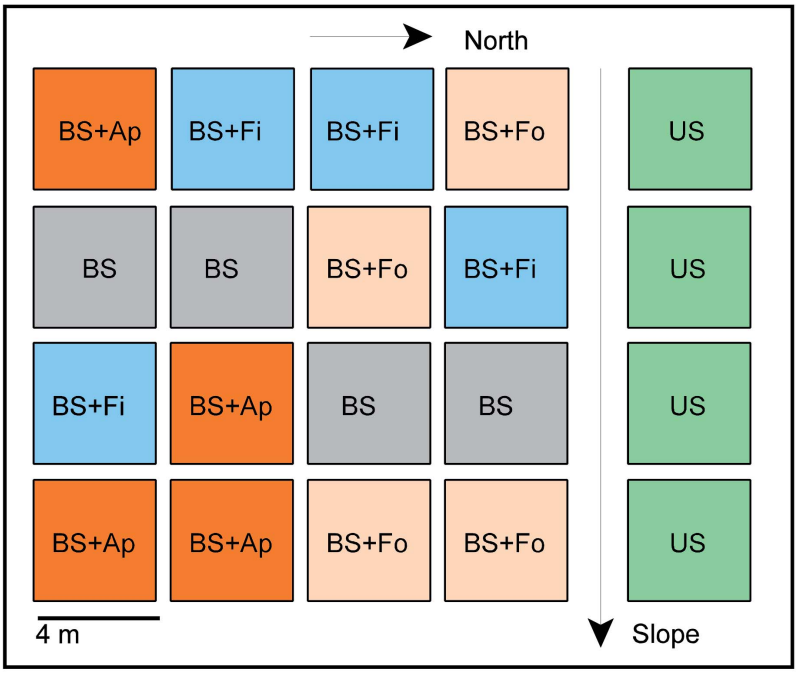

Figure 4.3: Plot distribution in the Tomiño study area. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foaming agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate.

soil was divided into fresh subsamples, which were kept at 4 ℃ for inorganic N measurements, and air-dried subsamples for the other analyses. For total N and δ^{15}N determination, aliquots of air-dried subsamples were finely ground (<100 μm) in a planetary ball mill (Retsch PM100, Retsch GmbH, Haan, Germany, with cups and balls of zirconium oxide). The presence or absence of the dominant shrub species (*Erica umbellata, Genista triacanthos, Pterospartum tridentatum, Ulex europaeus* and *Ulex micranthus*), as well as their maximum height, was recorded within each plot along three down-slope transects with sampling points every 25 cm (avoiding 50 cm on each plot-side to prevent possible edge effects). Plant material from the upper half of *Pinus pinaster* (50 pairs of needles from the youngest branches), *Ulex micranthus*, *Erica umbellata* and *Pterospartum tridentatum* (≈10 g of spines, leaves and twigs, and whorls respectively) was also collected (one composite sample per species per plot). *Genista triacanthos* and *Ulex europaeus* were not sampled because they were not analysed in the previous studies and they were lacking in some plots. The plant material was washed successively with tap and then deionised water, oven-dried at 60 ℃ for 48 h and finely ground in the same way as soils.

4.3.3 Methods

The dry matter content of soils and plant material was assessed by oven-drying sub-samples at 110 ℃ for 5 h. Soil pH was measured with a pH meter (Metröhm, Switzerland) in 0.1 M KCl employing a soil:solution ratio of 1:2.5. Total N and δ^{15}N of soils and plants were measured in ground samples with an elemental analyser (Carlo Erba, Milano, Italy) coupled on-line with an isotopic ratio mass spectrometer (Finnigan Mat, delta C, Bremen, Germany). An elemental reference material (Soil 3 from Eurovector, Milano, Italy) and isotopic standards (IAEA-N1 and IAEA-N2, alternately, from the International Atomic Energy Agency, Vienna, Austria) were included in each set of 10 samples to check the accuracy of the results; if necessary, drift correction was made against internal standards during the run. For soil NH_4^+-N and NO_3^--N analysis, an extraction-diffusion method described in Couto-Vázquez and González-Prieto (2006) was used, but with 48-h diffusion periods at 50 ℃; three blanks and three standards (NH_4NO_3) were included in each batch to subtract N from reagents and to check for N recovery. Instead of separate extraction with acetic acid for macronutrients and DTPA-$CaCl_2$-TEA for trace elements, as done in previous samplings of the study (Couto-Vázquez and González-Prieto, 2006; García-Marco and González-Prieto, 2008), soil Na, K, Mg, Ca, P, Al, Fe, Mn, Zn, Cu and Mo were jointly extracted by shaking soils for 2 hours with a solution of NH_4Ac 1 M and DTPA 0.005 M (soil:solution ratio 1:5). Compared with the respective traditional soil-tests, NH_4Ac-DTPA extracts similar quantities of Ca and higher amounts of K, Mg, Al, Cu, Fe, Mn and Zn (1.3x, 2.5x, 13x, 3x, 2.4x, 1.8x and 2.5x, respectively; S. García-Marco, pers. comm.). The soil extracts and the corresponding blanks were then filtered through cellulose paper (Filter-Laboratory 1242, 90-mm diameter) and analysed by simultaneous inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista Pro, Mulgrave, Australia). A calibration curve prepared with certified standards of all elements was measured beforehand and one of the calibration solutions was routinely included in each set of 30 samples as a quality control and, when

necessary, the calibration curve was measured again. In order to measure the total nutrient content of plant material, aliquots of 500 mg of plant samples were digested in a high performance digestion unit (Milestone 1200 Mega, Sorisole, Italy) for 55 min with 8 mL of 65% HNO_3 and 25 mL of 30% H_2O_2. Blanks and reference materials (hay powder No. 129, Community Bureau of References, EU; apple leaves No. 1515, National Institute of Standards and Technology, USA) were also included in each digestion batch to subtract elements from reagents and to check for element recovery. Once cooled, the solutions were filtered through quantitative filter paper (Filter-laboratory 1242, 90-mm diameter), transferred to 25 mL volumetric flasks, made to volume with water and analysed by ICP-OES as previously described for soils. Due to analytical interferences for determining total P in pine needles by this method, they were digested with HNO_3, HCl and H_2O_2 on a laboratory hot plate. The first day, 2 mL of HNO_3 70% were added to 150 mg aliquots of ground pine needles and the mixture was kept at room temperature for two days. Afterwards, 1 mL of HCl 37% was added, the sample tubes were slowly heated up to 130 ℃ and then the hot plate was turned off. The heating process was repeated twice (without the addition of HCl) the following two days. Then, the samples were treated with 4 mL of H_2O_2 30% (2 mL per day during two days) and slowly heated to 90 ℃. As for the other elements, blanks and reference material (hay powder No. 129, Community Bureau of References, EU) were also included in each digestion batch. The digested samples were transferred to 200 mL volumetric flasks, the pH was adjusted within the range 3 to 5 by adding NaOH pellets, made to volume with water and their total P content was measured by the method of Murphy and Riley (1962). Analytical-grade chemicals and type I water (ASTM, 2008) were used for analyses.

All analyses were carried out in duplicate and means were used in the statistical procedures, after doing a third analysis if the coefficient of variation was higher than 5 %. The effects of treatments on soil and plant variables 10 years after the prescribed fire were statistically analysed by one-way ANOVA. After checking the normal distribution of variables (Shapiro-Wilk's W test) and the equality of variances among treatment groups (Levene's test), significant differences among the group means were established at $p < 0.05$ using: (1) Tukey's test in the case of homoscedasticity of the original data (or data after Tukey's ladder of power or Box–Cox transformations); or (2) Games– Howell's test if variances remained heterogeneous after data transformations. All statistical analyses were performed with SPSS *15.0.* software (SPSS Inc., Chicago, IL).

4.4 Results

4.4.1 Effects of fire and FFCs on soil properties

Table 4.1 shows data on the main soil properties 10 years after the fire. No effect of fire or FFC on soil pH_{KCl} was found. Nitrate concentration was significantly higher in US plots (12 mg kg^{-1} dw) than in the burnt treatments (about 3 mg kg^{-1} dw) except for BS+Fi (6 mg kg^{-1} dw), while no differences among treatments in soil total N content, $\delta^{15}N$ and NH_4^+ were found. BS+Ap

plots had significantly more available P (14 mg kg^{-1} dw) than the other treatments (5 mg kg^{-1} dw). The concentration of Na was significantly higher in BS+Ap than in BS+Fi, with the other treatments having intermediate values, while no differences among treatments were found for Ca, K and Mg.

In unburnt soils, Fe concentration was significantly higher than in burnt soils. The available Mo differs slightly but significantly among treatments, being higher in BS+Ap, BS+Fi and BS than in US. For the available Al the only significant differences found were those among BS+Ap and BS+Fi plots (highest) and US (lowest). Neither the fire nor the addition of FFC affected the concentration of Cu, Mn and Zn.

Table 4.1: Effects of fire and firefighting chemicals on soil properties (mean ± S.D.) 10 years after the prescribed fire. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foaming agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate; dw, dry weight. Within each row, treatments with different letters are significantly different ($p < 0.05$).

	US	BS	BS + Fo	BS + Fi	BS + Ap
pH_{KCl}	3.16 ± 0.08^a	3.19 ± 0.02^a	3.24 ± 0.09^a	3.25 ± 0.06^a	3.12 ± 0.05^a
NH_4^+–N (mg kg^{-1} dw)	44.5 ± 6.2^a	41.9 ± 6.8^a	43.5 ± 6.1^a	42.9 ± 10.8^a	34.9 ± 3.1^a
NO_3^-(mg kg^{-1} dw)	12.1 ± 3.8^a	2.8 ± 1.5^b	3.5 ± 2.3^b	6.3 ± 2.9^{ab}	2.8 ± 0.4^b
Total N (mg kg^{-1} dw)	8.95 ± 1.48^a	7.92 ± 1.04^a	8.20 ± 0.51^a	7.71 ± 0.96^a	8.54 ± 0.68^a
δ ^{15}N (‰)	1.87 ± 0.25^a	1.73 ± 0.27^a	1.51 ± 0.21^a	1.59 ± 0.21^a	1.86 ± 0.33^a
Available Al (mg kg^{-1} dw)	194 ± 19^b	243 ± 15^{ab}	245 ± 32^{ab}	262 ± 23^a	269 ± 26^a
Available Ca (mg kg^{-1} dw)	118 ± 45^a	118 ± 48^a	119 ± 38^a	105 ± 47^a	69 ± 20^a
Available Cu (mg kg^{-1} dw)	0.55 ± 0.09^a	0.55 ± 0.12^a	0.60 ± 0.07^a	0.47 ± 0.06^a	0.58 ± 0.18^a
Available Fe (mg kg^{-1} dw)	900 ± 31^a	791 ± 14^b	796 ± 43^b	750 ± 48^b	723 ± 53^b
Available K (mg kg^{-1} dw)	95.3 ± 11.9^a	96.5 ± 15.3^a	103.3 ± 15.8^a	101.0 ± 21.8^a	92.0 ± 6.2^a
Available Mg (mg kg^{-1} dw)	76.7 ± 28.1^a	82.8 ± 30.2^a	86.0 ± 32.3^a	74.3 ± 32.1^a	56.5 ± 9.3^a
Available Mn (mg kg^{-1} dw)	3.73 ± 1.33^a	4.11 ± 1.68^a	3.91 ± 0.21^a	4.41 ± 0.50^a	4.18 ± 1.27^a
Available Mo (mg kg^{-1} dw)	0.44 ± 0.03^b	0.53 ± 0.03^a	0.53 ± 0.07^{ab}	0.56 ± 0.03^a	0.57 ± 0.04^a
Available Na (mg kg^{-1} dw)	38.0 ± 8.9^{ab}	31.0 ± 3.9^{ab}	36.0 ± 6.6^{ab}	28.3 ± 2.5^b	43.3 ± 6.7^a
Available P (mg kg^{-1} dw)	4.77 ± 0.21^b	4.68 ± 0.71^b	4.60 ± 0.43^b	5.15 ± 0.68^b	13.80 ± 1.24^a
Available Zn (mg kg^{-1} dw)	2.53 ± 0.64^a	2.46 ± 0.72^a	1.90 ± 0.18^a	3.34 ± 1.66^a	1.45 ± 0.51^a

4.4.2 Effects of fire and FFCs on plant elemental composition

Erica umbellata and *P. pinaster* had δ^{15}N values ranging from -3 to 0 ‰, whereas *P. tridentatum* and *U. micranthus* values were between -0.5 and 0.5 ‰ (Fig. 4.4). Significant differences among treatments for δ^{15}N were found in *U. micranthus* (BS and BS+Fo > US) and *P. pinaster* (BS+Ap > BS+Fi), while in *P. tridentatum* neither fire nor FFC effects were observed. For *E. umbellata* an additional test was done to compare BS+Ap with the other burnt treatments considered together, having the former significantly higher δ^{15}N values than the latter. Total N content of all the studied plant species was between 10 and 25 g kg^{-1} dw and was neither affected by fire nor by FFCs 10 years after the fire (Fig. 4.5).

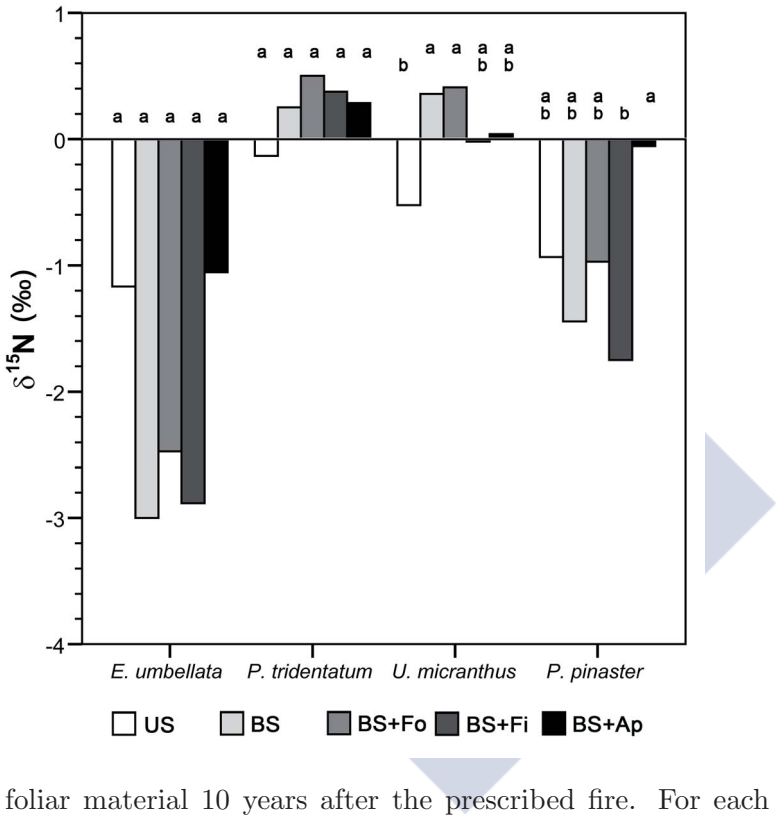

Figure 4.4: δ^{15}N in foliar material 10 years after the prescribed fire. For each plant species different letters indicate significant differences among treatments ($p < 0.05$). Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foaming agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate; dw, dry weight.

Regardless of the species, plant total P in BS+Ap plots was approximately twice as high as in the rest of the treatments ($p < 0.05$; Fig. 4.6). For plant total K (Fig. 4.6) significant differences were found between BS plots (higher) and BS+Ap plots (lower) in all shrub species and, moreover, in *P. tridentatum* all treatments were significantly higher than BS+Ap. In *P. pinaster* the highest K levels were found in BS+Ap and BS+Fi and the lowest in US and BS ($p < 0.05$). The highest Na levels were found in BS+Ap plots for *P. tridentatum* and *U. micranthus* and in US plots for *E. umbellata*, whereas in *P. pinaster* no significant differences due to either fire or FFCs were found (Fig. 4.6).

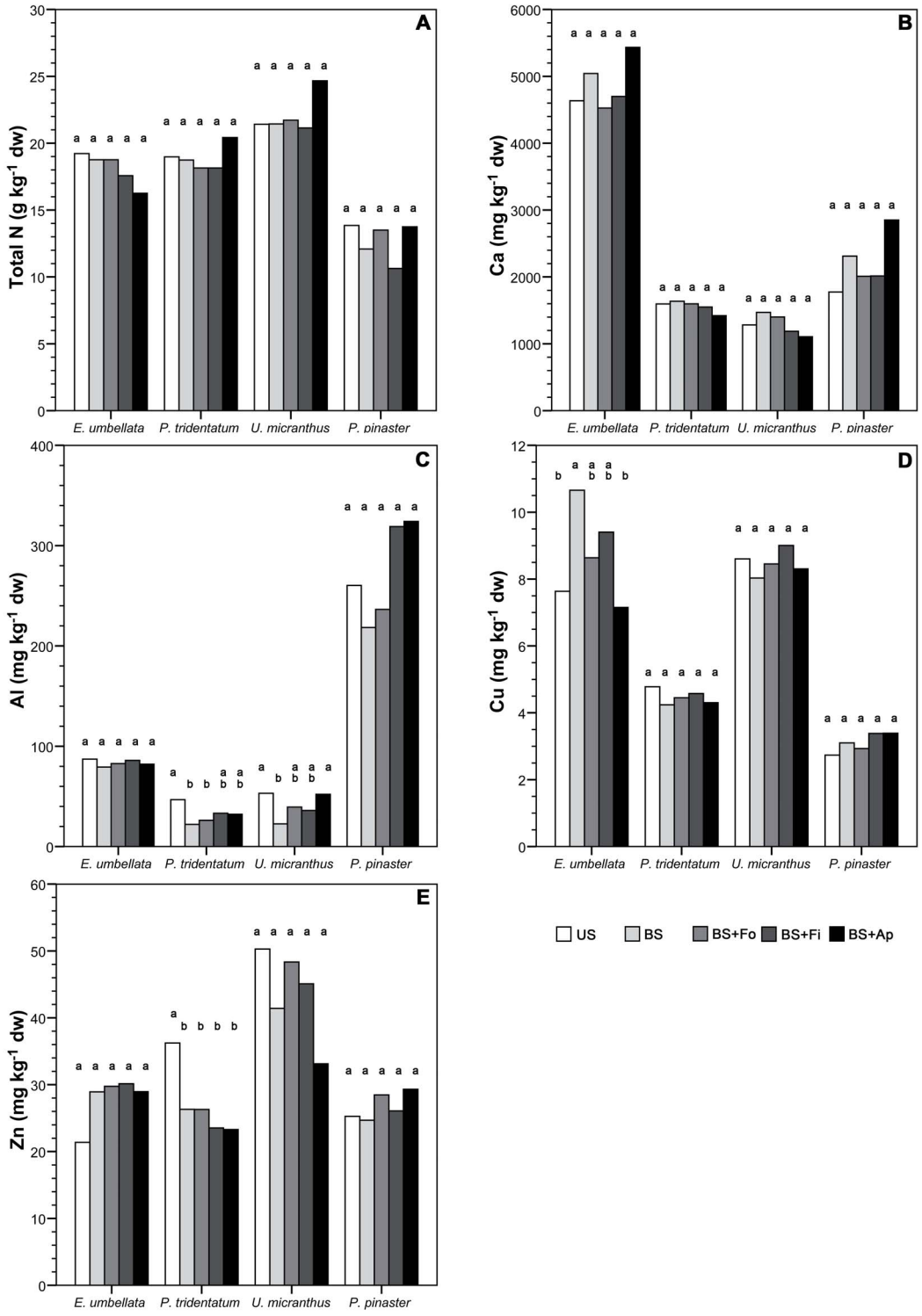

Figure 4.5: Plant total elemental concentration in foliar material 10 years after the prescribed fire of: a) N; b) Ca; c) Al; d) Cu and e) Zn. For each plant species different letters indicate significant differences among treatments ($p < 0.05$). Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foaming agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate; dw, dry weight.

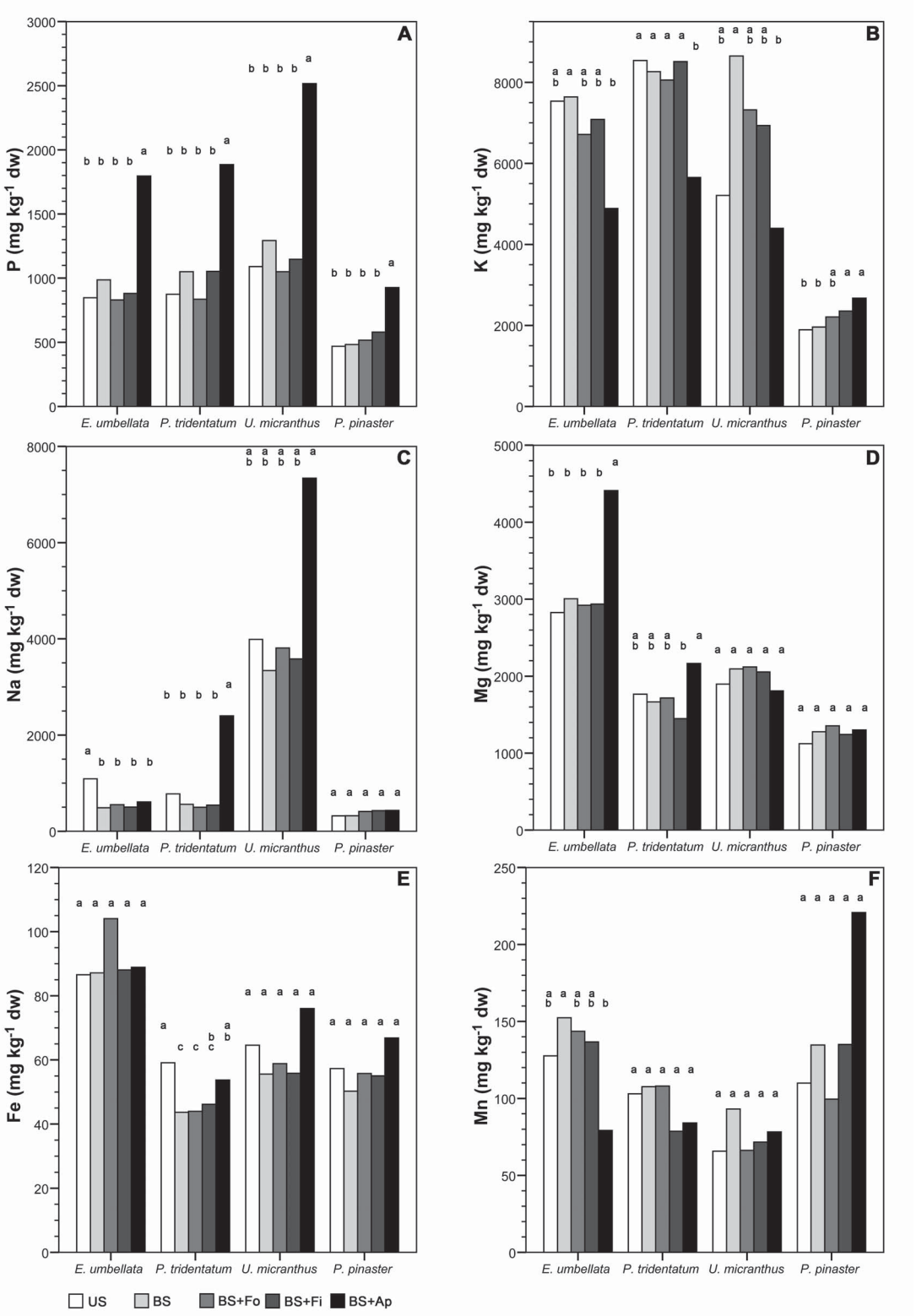

Figure 4.6: Plant total nutrient concentration in foliar material 10 years after the prescribed fire: a) P; b) K; c) Na; d) Mg; e) Fe; and f) Mn. For each plant species different letters indicate significant differences among treatments ($p < 0.05$). Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foaming agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate; dw, dry weight.

Whereas *U. micranthus* and *P. pinaster* showed no significant differences among treatments in plant total Mg, *E. umbellata* from BS+Ap plots had higher levels of Mg than plants from the other plots ($p < 0.05$), and *P. tridentatum* showed a similar tendency to that of *E. umbellata*, although differences were not always significant (Fig. 4.6). Plant total Ca was neither affected by fire nor FFCs in any of the studied species (Fig. 4.5).

Significant differences among treatments for Cu and Mn were only found in *E. umbellata* (Cu: BS > US ≈ BS+Ap; Mn: BS > BS+Ap) and for Fe and Zn in *P. tridentatum* (US > burnt treatments) (Fig. 4.5 and Fig. 4.6). Plant total Al (Fig. 4.5) was neither affected by fire nor FFCs in *E. umbellata* and *P. pinaster*, whereas small but significant differences were found in *P. tridentatum* (US > BS ≈ BS+Fo) and *U. micranthus* (US ≈ BS+Ap > BS). Molybdenum concentration was close to the detection limits in shrubs and in pines and its variance was very high and heterogeneous (data not shown).

4.4.3 Effects of fire and FFCs on vegetation cover

Pines growing in BS+Ap plots were the tallest and had the largest basal diameter, followed by pines from US, BS+Fi, BS+Fo and BS for both variables (Fig. 4.7). The highest pine mortality was in BS+Fi plots (only half of the 16 planted pines were alive at t=10 years). In BS+Ap plots less pines had died (3 out of 16), but 5 had distorted trunks. In US, BS and BS+Fo the pine mortality was lower (3, 3 and 2 dead pines respectively). Although almost 25% of the pines had died by t=10 years, there were only one BS+Fi and one BS+Ap plot without living pines. Between years 5 and 10 after the fire, two pines from a US plot died and the trunks of 5 pines from BS+Ap plots became distorted.

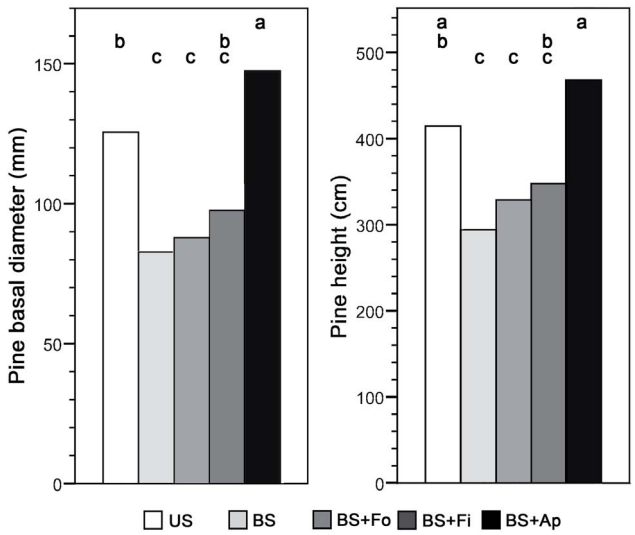

Figure 4.7: Basal diameter (a) and height (b) of *P. pinaster* 10 years after the prescribed fire. Different letters indicate significant differences among treatments ($p < 0.05$). Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foaming agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate.

Figures 4.8 and 4.9 show cover and height of the studied shrubs. Ten years after the fire, both plant cover and height of *E. umbellata* were significantly lower in BS+Ap plots (plant cover around 30%; mean height 60 cm) than in the other treatments (plant cover > 85%; mean height 70-80 cm). *Genista triacanthos*, not previously recorded in the experimental plots or the surrounding area, appeared in plots of all treatments except BS+Ap and covered 7-19% of soil surface with a mean plant height between 70 and 90 cm, without significant differences in any of the two variables among treatments. For *P. tridentatum* the plant cover ranged between 40% and 95%, being significantly higher in BS+Ap plots, and mean plant height was around 70-90 cm without significant differences among treatments. *Ulex europaeus* covered a small proportion of the soil (< 10%) but these plants were the tallest among the shrubs (90 to 150 cm). There were no significant differences in *U. europaeus* cover among treatments and no statistical analysis could be done for its height (this species was only present in 8 plots). The cover of *U. micranthus* was between 20% and 50%, decreasing in the order BS+Fo, BS, BS+Fi, BS+Ap and US, while its mean height ranged from 70 to 90 cm and did not differ significantly among treatments.

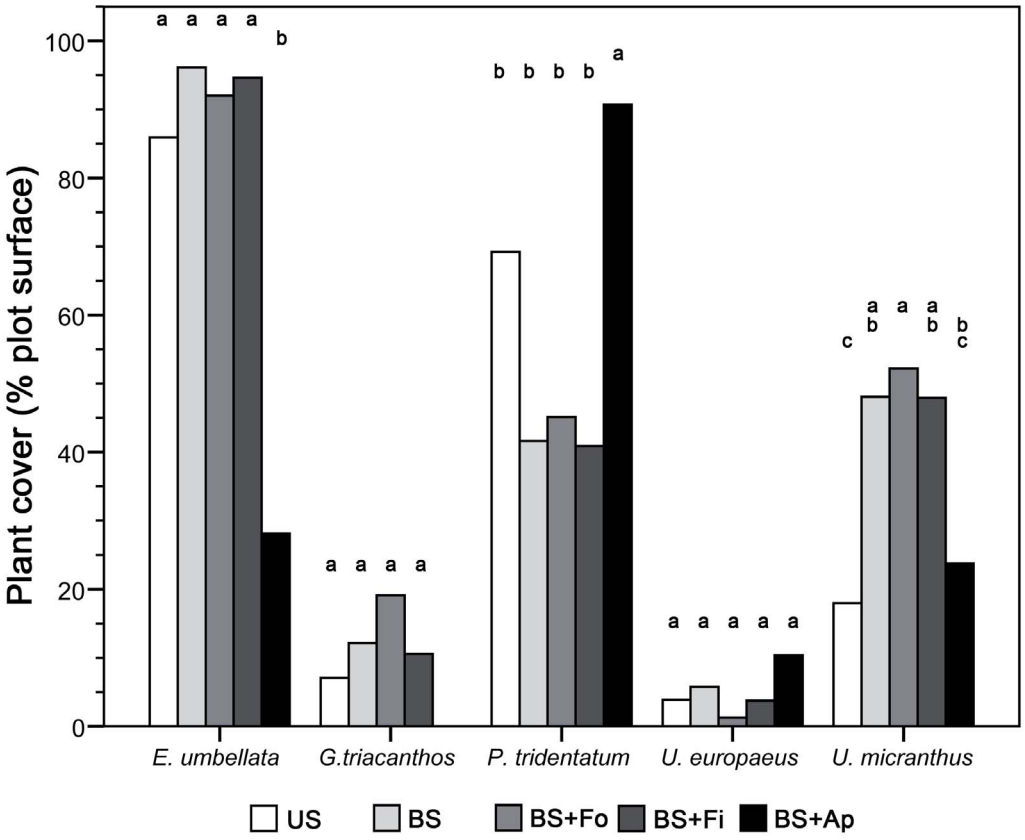

Figure 4.8: Plant cover of the shrub species 10 years after the prescribed fire. For each shrub species different letters indicate significant differences among treatments ($p < 0.05$). Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foaming agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate.

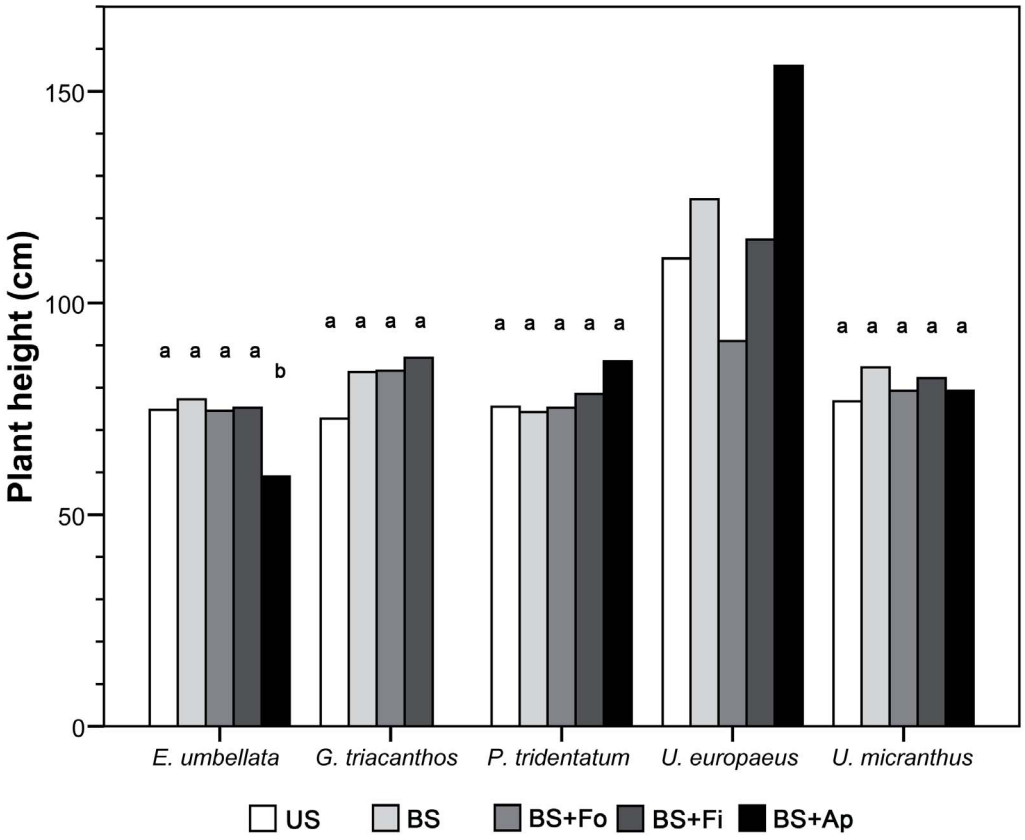

Figure 4.9: Plant height of the shrub species 10 years after the prescribed fire. For each shrub species different letters indicate significant differences among treatments ($p < 0.05$). For *U. europaeus* no statistical analysis could be done because it was only present in 8 plots. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foaming agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate.

4.5 Discussion

4.5.1 Effects of fire and FFCs on soil properties and plant elemental composition

During the first post-fire months Couto-Vázquez and González-Prieto (2006) reported significantly higher soil pH_{KCl} in burnt plots, which resumed to pre-fire values after one year. Five years after the fire all plots became significantly acidified compared to t=0 (Couto-Vázquez et al., 2011) and no subsequent changes were recorded after 10 years. As the area of the field experiment is under a high grazing pressure and the plots were fenced after the prescribed fire, Couto-Vázquez et al. (2011) attributed the soil acidification to grazing exclusion as also reported in other studies (Basher and Lynn, 1996; Dormaar and Willms, 1998).

Although the meta-analysis done by Johnson and Curtis (2001) showed a significant positive effect of fire on soil N 10 years after the fire, in our case it was fairly constant throughout the

whole field experiment. The higher total N concentration in plants from BS+Ap plots recorded at t=5 years (differences not significant for all species; Couto-Vázquez et al. (2011)) contrasted with the lack of significant differences 10 years after the fire; indeed, *E. umbellata* from the BS+Ap treatment had the lowest total N content. Therefore, it can be concluded that the N-fertilizing effect that ammonium polyphosphate had on the studied species during the first 5 years is not noticeable 10 years after the fire, likely due to the substantial N leaching as Pappa et al. (2006) and Pappa et al., (2008) reported in pots added with an N- and P-based FFC.

After an increase of soil δ^{15}N in burnt soils during the first post-fire year, attributed to N losses triggered by the fire (Couto-Vázquez and González-Prieto, 2006), soil ^{15}N abundance increased in all treatments at t=5 years (Couto-Vázquez et al., 2011) and decreased at t=10 years but remained higher than pre-fire levels. The lack of differences among treatments both five and 10 years after the fire suggests that factor(s) other than fire or FFCs are influencing the soil δ^{15}N, possibly changes in the N cycle of the soil-plant system due to grazing exclusion. For most species, plant δ^{15}N values increased slightly from five (Couto-Vázquez et al., 2011) to 10 years after the fire, although differences among treatments more or less prevailed for all species. In shrubs there were no differences in *P. tridentatum*, small differences in *U. micranthus* and significant differences among burnt treatments in *E. umbellata* due to ammonium polyphosphate addition. In *P. pinaster* the BS+Ap plots showed the highest δ^{15}N values at t=10 years, as at 5 years earlier, but differences with the other treatments were no longer significant except for BS+Fi.

Both *E. umbellata* and *P. pinaster* can establish mycorrhizal symbioses that lead to ^{15}N-depleted plants and ^{15}N-enriched fungi due to a strong isotopic fractionation (West et al., 2006). The high δ^{15}N values recorded for BS+Ap plots and the positive correlations between δ^{15}N and total plant P in these species ($r = 0.535$ to 0.655; $p < 0.02$) suggest that, even 10 years after the application of ammonium polyphosphate, the N transfer from the fungi to the plants was affected by either: a) a reduction in soil mycorrhizal abundance; or b) a rise in the direct uptake of soil N by pines, probably because ammonium polyphosphate addition increased the labile soil N pool even in the long-term.

The soil NH_4^+-N concentrations varied greatly with time (especially in BS+Ap plots) but at t=10 years they were similar among treatments and to prefire levels. Contrastingly, from one to 10 years after the fire the NO_3^--N levels were higher in unburnt than in burnt plots (except BS+Ap at t=5 years); therefore, data from the present study suggests a decrease of net nitrification in the burnt soil even in the long-term. As highlighted by Gómez-Rey and González-Prieto (2013), published results about the effects of fire on gross and net nitrification are contradictory, with some studies reporting a decrease in post-fire nitrification (see Bastias et al. (2006) and references therein) and others the opposite (DeLuca et al., 2006; Kaye and Hart, 1998; Koyama et al., 2010; Koyama et al., 2012).

Despite a marked decrease with respect to the 24-fold higher values recorded at t=5 years (Couto-Vázquez et al., 2011), the available P in BS+Ap soils was still three times higher

than in the other treatments 10 years after the fire. Total P in plants from BS+Ap plots was approximately twice as high as in the other treatments both 5 and 10 years after the fire (Couto-Vázquez et al., 2011). Several authors have suggested that the application of P-based fire retardants could have long-lasting effects on soil and plant P and therefore long-term studies of at least 10 years are needed (Giménez et al., 2004; Larson et al., 1999). Our results filled this gap of knowledge showing a significant effect of the ammonium polyphosphate treatment on soil available and plant total P concentrations even 10 years after the fire. Therefore, despite the substantial P leaching reported after adding an ammonium polyphosphate based FFC (Pappa et al., 2006; Pappa et al., 2008), our results showed that the remaining amount of P was enough to substantially modify the availability and plant uptake of these nutrients for a long time.

The high concentration of soil P in BS+Ap plots was the main and most long-lasting factor affecting vegetation development during the experiment, although other factors such as pH, available N and certain nutrient ratios (Fe/Mn, P/Fe, P/Zn) have also played an important role in earlier stages (Couto-Vázquez et al., 2011; Couto-Vázquez and González-Prieto, 2006; García-Marco and González-Prieto, 2008). For the leguminous species (*P. tridentatum* and *U. micranthus*) there was a positive correlation between plant total N and P ($r = 0.621$ to 0.691; $p < 0.005$). Although contradictory results have been reported about the effects of P fertilisation on N_2 fixation rates in legumes (see Cavard et al. (2007) and references therein), the N-P correlation we found could be due to an enhanced N_2 fixation due to P fertilisation because BNF is a P-demanding process (Rodríguez-Echeverría et al., 2009).

For soil Na, we found a significant and unexplained difference, not reported 5 years before, between BS+Ap (highest) and BS+Fi (lowest), and no significant differences among treatments for soil K. Nevertheless, the Na/K ratio in *P. tridentatum* and *U. micranthus* was significantly higher in BS+Ap plots than in the other treatments both at t=5 years (based on data from Couto-Vázquez et al. (2011)) and t=10 years. Therefore, the addition of ammonium polyphosphate probably had an influence on the Na/K ratio of the leguminous plants, although no information regarding how P availability affects the mechanisms of Na and K regulation in legumes has been found. Moreover, *E. umbellata* in BS+Ap plots showed the lowest concentration of K (without significant differences in the Na/K ratio) and Mn, as well as the highest Mg concentration. Again, the ammonium polyphosphate seems to have an impact on plant nutrition of this species, although more data and information are needed to ascertain the mechanisms involved.

A short-term decrease in available Fe has usually been reported after wild and prescribed fires (Certini, 2005; Close et al., 2011; García-Marco and González-Prieto, 2008; Gómez-Rey et al., 2013a; González-Parra et al., 1996). Results from our study site showed that this fire-derived Fe depletion is a long-lasting effect, as both five years (Couto-Vázquez et al., 2011) and 10 years after the fire the unburnt soil had 10-18% more available Fe than the burnt treatments. Plant total Fe 10 years after the fire showed no significant differences among treatments for all species except *P. tridentatum*, as also reported 5 years earlier (Couto-Vázquez et al., 2011). However, if all the species are considered together, Fe concentration in plants from BS+Ap plots was significantly

higher than in BS ($p < 0.05$), being intermediate in the other treatments. Although burnt soils tend to be depleted in Fe compared to unburnt soils (García-Marco and González-Prieto, 2008), soil Fe availability in the study area seems to be high enough to preclude a fire-triggered Fe deficiency in plants. However, if the long-term decrease we found in available Fe concentration is also a rule in burnt soils, forest fires would pose a fertility problem in ecosystems with low levels of this nutrient, as previously suggested by García-Marco and González-Prieto (2008).

For the other elements (Ca, Cu, Al and Mo) no clear effect of fire or FFCs was observed. In the case of soils, the available Al and Mo were strongly correlated ($r= 0.964$; $p< 0.001$), suggesting that the available Mo, which is an essential constituent of enzymes involved in the N cycle (Fageria et al., 2002; Williams and Fraústo da Silva, 2000), could be associated to Al (oxy) hydroxides.

4.5.2 Effects of fire and FFC on vegetation cover

The pines with the best trade-off between size and survival were those in the unburnt plots (second highest and widest pines, second lowest mortality). The significant differences in pine height and basal diameter among US and BS treatments indicate that the negative effect of fire on pine growth already reported during the first 5 years (Couto-Vázquez et al., 2011) persisted even 10 years after the fire. The BS+Fo and BS+Fi treatments did not show any effects on pine growth, but the highest pine mortality was recorded in the BS+Fi plots, as for 5 years before (Couto-Vázquez et al., 2011). At t=10 years, pines in BS+Ap plots were the biggest, both in height and diameter (as for 5 years after the fire, see Couto-Vázquez et al. (2011)), although they had the second highest mortality and one third of them were clearly distorted (useless for timber production) and probably no longer viable; a problem that was recorded neither 5 years earlier in BS+Ap plots nor at t=10 years in the other plots. Ammonium polyphosphate based FFCs are known to have a fertilizing effect on pines (Couto-Vázquez et al., 2011; Pappa et al., 2008); however, lower relative amounts of root tissue in response to high resource conditions have previously been reported (see Coleman (2007), and references therein). These results suggest that the problem we found in BS+Ap plots could originated from an unfavourable shoot-to-root ratio due to the high amount of N and P supplied by the ammonium polyphosphate. If this hypothesis is correct, the root system of BS+Ap pines could be insufficient to sustain the trunks beyond a certain size, when the wind would bend the pines over at the root neck leading to a distorted growth form.

Compared to the shrub data obtained 5 years after the fire (Couto-Vázquez et al., 2011), the cover of: a) *E. umbellata* decreased in BS+Ap plots and increased slightly in the others; b) *P. tridentatum* increased in all treatments; c) *U. micranthus* decreased in BS+Ap and US, whereas it increased in BS, BS+Fo and BS+Fi; and d) *U. europaeus* decreased in BS+Ap, increased in BS and was detected for the first time in the other treatments. While at t=5 years plants in BS+Ap plots were significantly higher than those growing in the other treatments, 5 years later there was either no difference among treatments (*P. tridentatum* and *U. micranthus*) or plants

growing in BS+Ap were smaller than the others (*E. umbellata*). At t=10 years *G. triacanthos* was recorded for the first time in all treatments except BS+Ap.

Ten years after the fire, no fire effect on shrub cover or height was found except for a higher cover of *U. micranthus* in BS compared to US plots. Regarding FFCs, the data indicates that BS+Fi and BS+Fo have no long-term effects on plant communities, consistent with observations for another foaming agent (Larson et al., 1999), whereas the BS+Ap treatment still affected the shrub community, apparently preventing the development of *E. umbellata* and the establishment of *G. triacanthos*. Negative effects of ammonium polyphosphate on seed germination and viability have already been reported (Cruz et al., 2005; Luna et al., 2007; Song et al., 2014), although it has been suggested that its effect on plants is negligible under field conditions (Song et al., 2014) or that it might disappear once the retardant is gone (Angeler et al., 2004). However, our data shows that the BS+Ap treatment still had an effect on some soil and plant properties 10 years after its application, as P concentration in the BS+Ap plots was still three times higher in soils and two times higher in plants than in the other treatments. The shrubs *G. triacanthos* and *E. umbellata* are the only obligate seeders studied in the experiment (Reyes et al., 2009) and therefore the most sensitive to hampered germination due to the application of ammonium polyphosphate. In contrast, *U. europaeus*, *U. micranthus* and *P. tridentatum* are strong resprouters (Reyes et al., 2009) and they had benefited from the fertilizing effect of the fire retardant up to 5 years after the prescribed fire (Couto-Vázquez et al., 2011). Nevertheless, data from t=10 years (shorter *P. tridentatum* plants; lower cover of *U. europaeus* and *U. micranthus*; high soil and plant P levels) suggests that the fertilizing effect was counterbalanced by other side effects of ammonium polyphosphate.

Although plant cover data from this study should be cautiously compared with that in the pre-fire plant survey (Pesqueira et al., 2005) as the latter is not given in a quantitative form, two differences must be highlighted: a) *G. triacanthos* appeared in our plots (except BS+Ap) between 5 and 10 years after the fire; and b) the coverage of *Ulex micranthus* was larger than that of *U. europaeus* in our experimental plots, while the reverse was true in the surrounding area. These differences cannot be attributed to the fire or the fire-fighting chemicals, because they were also observed in the control unburnt plots. As our experimental plots were fenced but the surroundings were under a high grazing pressure, we hypothesize that grazing exclusion is an important factor influencing the plant communities growing in the area. On the one hand, grazing is a selective perturbation for plant communities as it often exerts a higher pressure on legumes due to their higher nutrient content (Pesqueira et al., 2005) and, thus, grazing exclusion may favour the establishment of *Genista triacanthos*. On the other hand, *U. micranthus* with weaker spines seems to be more palatable than *U. europaeus*.

Competition between different shrub species could also have shaped the plant community in the experimental plots. Irrespectively of the treatment, the resprouter species need less time to recover after the fire than the obligate seeders (Calvo et al., 2002; Pesqueira et al., 2005) and, therefore, the former (*U. europaeus*, *U. micranthus* and *P. tridentatum*) can displace the latter (*E. umbellata* and *G. triacanthos*). In the BS+Ap treatment, the obligate seeders were at a

disadvantage due to the negative effect of ammonium polyphosphate on seed germination and viability (Luna et al., 2007), whereas the resprouters did not suffer this deleterious impact and were favoured by the fertilizing effect in the medium- to long-term (Couto-Vázquez et al., 2011).

To conclude, the main effects after 10 years of the experimental fire in the soils were a reduction in nitrate levels and Fe availability, although no symptoms of plant Fe deficiency were detected, likely due to the iron-rich soils. Concerning the vegetation, it is noteworthy that the 10-year-old pines still showed the negative effects of the prescribed fire on their growth. No other remarkable effects of the fire on the soil-plant system were found. Among the studied fire-fighting chemicals, the only one with long lasting effects was ammonium polyphosphate, which even 10 years after its application had profound effects on the ecosystem: a) increased the concentrations of soil available and plant total P; b) depressed K uptake in shrubs and increased Na uptake in legumes; c) reduced pine's viability; d) modified the species composition of the shrub community (obligate seeders hindered by resprouters); and e) played an important role in N nutrition in plants, probably by affecting their mycorrhizal (*E. umbellata* and *P. pinaster*) and rhizobial (*U. micranthus* and *P. tridentatum*) symbioses.

Section 5

Straw mulching is not always a useful post-fire stabilisation technique for reducing soil erosion

Section 5 is based on the following paper:

Fernández-Fernández, M., Vieites-Blanco, C., Gómez-Rey, M.X., González-Prieto, S.J. (2016) Straw mulching is not always a useful post-fire stabilization technique for reducing soil erosion. *GEODERMA* 284, 122-131.

5.1 Abstract

Mulching is increasingly employed to stabilize burnt areas, making necessary to elucidate where and how it should be used. The effects of mulching and the efficiency of two straw application strategies in reducing nutrient losses were evaluated in a steep area (burnt with moderate severity) with twelve experimental plots split into three sets: control burnt plots (BS), burnt plots with straw mulching in narrow bands along the contour lines (NM, global dose 800 kg ha^{-1}) and in wide bands (WM, global dose 1000 kg ha^{-1}). None of the mulching strategies had a significant effect on most of the 16 soil and sediment variables analysed (pH, nutrient and trace element concentrations). The principal component analyses show that soil and sediment samples change with time after the fire regardless treatment, decreasing progressively the differences between successive sampling dates. In sediments, pH_{KCl}, Ca, Mg, Mn and Zn fitted to curvilinear regression models with time after fire as independent variable, while the other variables showed no clear temporal trend. During the first post-fire year, less than 500 kg ha^{-1} of sediments were eroded and mulching had no effect on the total mass of lost sediments and nutrients. We conclude that the erosion rate was rather low that year due to moderate precipitation rates and therefore mulching did not significantly reduce soil erosion. Nevertheless, the concentration of Mo, Mn and Zn in sediments exceeded reference levels for ecosystem protection and can lead to deficiency problems for on-site vegetation and to soil and water pollution off-site.

5.2 Introduction

Fire is a global phenomenon affecting more land area than any other natural disturbance (Bento-Gonçalves et al., 2012) and one of the major causes of forest destruction and soil degradation (Certini, 2005; Shakesby, 2011). Although fire is a natural driving force in some ecosystems, humans are responsible for most of the current large-scale and intense wildfires (Bento-Gonçalves et al., 2012). In the foreseeing scenarios of climate change and a drastic shift in land use due to rural exodus and socio-economic factors, the number and severity of wildfires will probably increase substantially (Bento-Gonçalves et al., 2012; Birot, 2009; Pereira et al., 2011). Lately, extensive research on the effects of fire on soil properties has been done (see list of comprehensive reviews in Bento-Gonçalves et al. (2012)). The impacts on soils depend on fire severity (duration and intensity), frequency, as well as on the season of fire occurrence and the characteristics of the forest floor (Bento-Gonçalves et al., 2012; Certini, 2005). Accordingly, fire effects on the soil can either be reversible or permanent, being climate, vegetation and topography of the burnt area the factors controlling the resilience of the soil system (Certini, 2005). Wildfires often reduce the amount of organic matter in the soil, alter its structure, modify soil biological communities and increase nutrient losses through volatilisation, ash entrapment in smoke columns, leaching and erosion (Shakesby, 2011). Research on the effects of fire on soil chemical quality has been mainly focused on assessing the changes in SOM and available macronutrients, and to a lesser extent on micronutrients and trace elements.

Fires lead to an immediate increase in soil concentrations of most nutrients and trace elements due to the substantial quantities of these elements present in ashes from burnt vegetation and also to the release from SOM after its breakdown by the fire (Certini (2005) and references therein). Fire effects on soil nutrients and trace elements may last for a few months or for years, depending on how fast they are lost from soil (or taken up by plants). Nutrient losses are conditioned by the solubility of the elements in ashes (Certini, 2005) and by the erosion rate, which is highly dependent on the percentage of bare-ground areas and the post-fire weather pattern (Thomas et al., 1999).

Although SOM losses are the most common phenomena in the short-term (Certini, 2005; Certini et al., 2011; Couto-Vázquez and González-Prieto, 2006; Gómez-Rey and González-Prieto, 2014), increases of SOM in the long term have also been reported in several experiments (meta-analysis by Johnson and Curtis (2001)). The main effects of wildfires on the N cycle are: a significant removal of organic N due to SOM combustion; a redistribution of the remaining soil organic N; the conversion of organic to inorganic N; losses due to leaching, erosion and volatilisation; and a marked alteration of both quantity and specific composition of microbial communities (Certini, 2005; Fisher and Binkley, 2000; Prieto-Fernández et al., 2004). Increased soil inorganic N concentrations after fires have been widely reported. Both measurements of ^{15}N natural abundance in soils and plants (Aranibar et al., 2003; Couto-Vázquez and González-Prieto, 2006) and ^{15}N-tracing experiments have been used to study the effects of burning on the N cycle (Gómez-Rey and González-Prieto (2013) and references therein), but no common response of gross N transformations to fires was found, most probably due to the large number of influencing factors. Organic P in soils is depleted by fire at a higher rate than the supplied from mineral weathering (DeBano et al., 1998); however, burning is also responsible of the transient increase in P availability resulting from the mineralisation of organic P to orthophosphate (Cade-Menun et al., 2000; Saá et al., 1994).

Fewer studies have assessed the effects of burning on soil micronutrients and trace elements, although they are essential for plant development and post-fire changes in their soil availability could lead to deficiencies or toxicity effects on plants (García-Marco and González-Prieto, 2008; Gómez-Rey et al., 2014). The scarce available data on micronutrients and trace elements in burnt ecosystems is often contradictory due to the differences among the studies in terms of fire type and characteristics (wild or prescribed, severity and frequency), climate conditions, vegetation cover, soil type and sampling design (soil/ash/sediment samples, time after the fire, fraction of the elements measured) (Brye et al., 2002; Close et al., 2011; García-Marco and González-Prieto, 2008; Gómez-Rey et al., 2013a; González-Parra et al., 1996; Pereira et al., 2011; Pivello et al., 2010; Ponder et al., 2009; Stankov-Jovanovic et al., 2011).

Erosion is widely recognized as a common process after wildfires (DeBano et al., 1998; Robichaud and Brown, 1999) and post-fire erosion effects on downstream water quality and sedimentation are recognised (Smith et al., 2011). However, it is still controversial whether nutrient losses in eroded sediments affect the long-term soil quality and site productivity (Baird et al., 1999; Gómez-Rey et al., 2013b; Gómez-Rey et al., 2014; Robichaud et al., 2006; Shakesby

et al., 2002; Thomas et al., 1999). Although studies have been mainly focused on nutrient losses in solution rather than on losses with the eroded material (de Koff et al., 2006), nutrients attached to sediments can substantially exceed those lost in solution (Gimeno-García et al., 2000; Smith et al., 2011). Reported annual post-fire erosion rates are highly variable, ranging from 1 to 240 Mg ha^{-1} (Moody and Martin, 2009; Robichaud et al., 2006), as they depend on fire intensity, climate, topography and vegetation of the site, the percentage of bare soil and its infiltration capacity (Fisher and Binkley, 2000; Vega et al., 2005). The greater the intensity of the fire, the higher the amount of nutrients found in eroded sediments (Andreu et al., 1996; Gimeno-García et al., 2000), although high nutrient losses in sediments have also been reported in low intensity fires (de Koff et al., 2006; Gómez-Rey et al., 2013b; Gómez-Rey et al., 2014). Usually, the greatest nutrient losses are recorded within the first 4-12 months after the fire and they generally decrease by an order of magnitude per year (Gómez-Rey et al., 2013b; Gómez-Rey et al., 2014; Robichaud et al., 2000; Robichaud et al., 2006).

Different measures have been implemented after wildfires to minimize fire impacts (Bento-Gonçalves et al., 2012). Post-fire stabilisation techniques must be applied as soon as possible after a wildfire, especially when the vegetation cover is completely destroyed, in order to prevent surface runoff and erosion and to accelerate development of vegetation cover (Robichaud, 2009; Robichaud et al., 2000; Vega et al., 2005). Besides seeding of fast-growing grass species, the most effective and widely used BAER technique is straw mulching (Bento-Gonçalves et al., 2012), which has shown an immediate effectiveness in increasing ground cover and thus it alleviates erosion during the first critical months after the fire (Bautista et al., 2009; Díaz-Raviña et al., 2012; Groen and Woods, 2008; Robichaud et al., 2010).

Until recently, the available information about the effects of post-fire straw mulching on chemical properties of soils and sediments was very scarce (Díaz-Raviña et al., 2012; Fontúrbel et al., 2012). Mulching can alter the MIT (by supplying a substrate with high C/N ratio), enhance vegetation recovery (and thus nutrient uptake by plants), modify the runoff-infiltration ratio, or preferentially reduce the erosion of some soil fractions; consequently, this stabilisation technique could alter the chemical composition of soils and sediments. However, some studies have already shown that mulching does not affect the nutrient concentrations in soils and sediments when compared to a control burnt soil, but it does effectively reduce erosion. For instance, Vega et al. (2014) conducted a prescribed fire in a steep area with rainy climate and concluded that erosion was significantly reduced by straw mulching on burnt plots during the first year. A similar experiment carried out in another steep area (up to one year after a wildfire) showed that mulching did not modify the concentration of nutrients in soils, mulched plots were more similar to the unburnt control than burnt plots without mulching, and straw addition resulted in a short-lived stimulation of gross mineralisation and gross immobilisation of ammonium (Gómez-Rey and González-Prieto, 2014; Gómez-Rey and González-Prieto, 2015).

Despite the fact that Galicia (NW Spain) has a temperate-humid climate, it is one of the European regions with the highest fire incidence (Birot, 2009). The causes are a complex mixture of traditional use of fire as a silvopasture agroforestry tool, deep economic and demographic

changes in rural areas and incendiarism as protest (Gómez-Rey et al., 2013a). In a region with such a large area affected by wildfires, the compromise among applying straw to burnt soils in order to prevent erosion, the costs and difficulties of its application in large or remote burnt areas and the potential competence with other uses (livestock fodder) of this limited resource arises as a controversial issue. Therefore, it is paramount to elucidate where and how is convenient to use straw mulching as a BAER technique. To ensure the 60-70% of ground cover needed to effectively protect the burnt soil against erosion (Robichaud, 2009), straw doses of 2300-2500 kg ha^{-1} have been used in Galicia (Díaz-Raviña et al., 2012; Fernández et al., 2011; Fernández et al., 2012; Gómez-Rey et al., 2013a). Instead of mulching the entire burnt area, a possible strategy to reduce these doses could be to apply the straw on bands along the contour lines alternating with bands without straw. In such a design, we need to determine how wide the mulched bands should be to effectively protect the unmulched bands against the erosion. The aims of the present study (Fig. 5.1), conducted in a steep area affected by a medium severity wildfire, are: a) to evaluate the effects of straw mulching on soil and sediment properties; and b) to assess the efficiency of two straw mulching application strategies (narrow and wide bands along the contour lines leading to global straw doses of 800 and 1000 kg ha^{-1}, respectively) to reduce nutrient losses in eroded sediments.

5.3 Material and methods

5.3.1 Site description and experimental design

The study area was located in Saviñao (Lugo, NW Spain; 29T $^{06}13$ $^{47}24$, 510-530 m a.s.l.; Fig. 5.2), under temperate (mean annual temperature 12.7 ºC) and moderately rainy climate (827 mm y^{-1}). In September 2012 a medium severity wildfire burnt 85 ha of forest and shrubland and twelve plots were set up in an experimental field of 1.3 ha within the shrubland area with homogeneous slope (33-38%), orientation (S-SW), soil type (Umbric Leptosol developed over slates) and vegetation cover (dominated by the shrubs *Cytisus striatus*, *Erica arborea*, *Ulex europaeus* and *Pterospartum tridentatum*). As it was a wildfire, all plots were distributed in the only suitable homogeneous area found in the whole burnt zone (see Fig. 5.2) and, thus, pseudoreplication can restrict the generalisation of our results. The plots were 40x10 m each, with the longest dimension parallel to the maximum slope. To monitor post-fire erosion, the plots were delimited upwards and downwards by a geotextile fabric fixed to posts following the design suggested by Robichaud and Brown (2002). One month after the fire, three treatments were arranged in a fully randomized design with four replications (Fig. 5.3): a) control (BS), burnt plots without any stabilisation treatment; b) wide mulching (WM), burnt plots with straw applied in the upper half of the plot at 200 g m^{-2} (global plot dose: 1000 kg ha^{-1}); and c) narrow mulching (NM), burnt plots with straw applied in two alternated 8 m wide bands at 200 g m^{-2} along the contour line (global plot dose: 800 kg ha^{-1}).

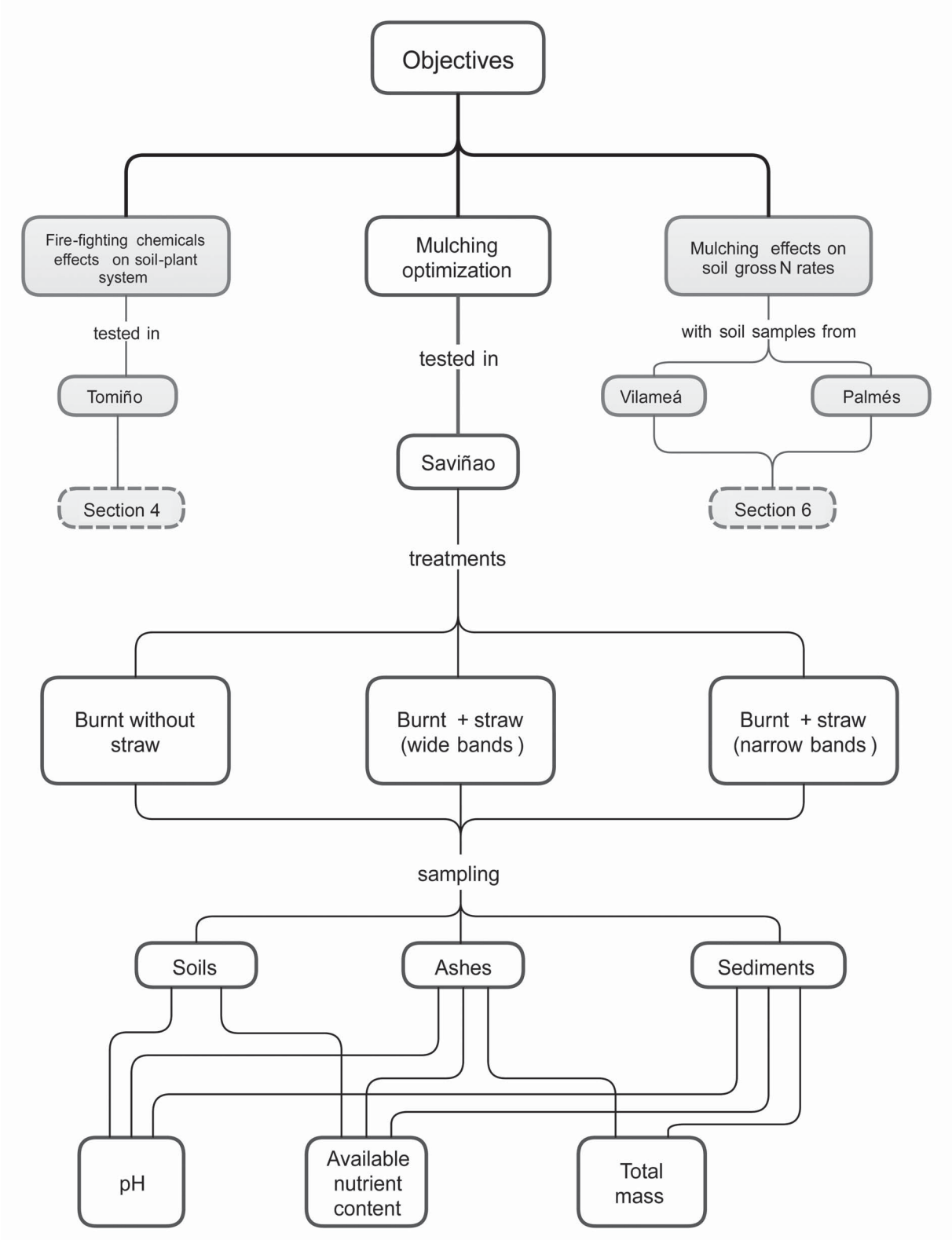

Figure 5.1: Schematic representation of the main objectives of the thesis, highlighting the specific aims, treatments and analyses of the current section.

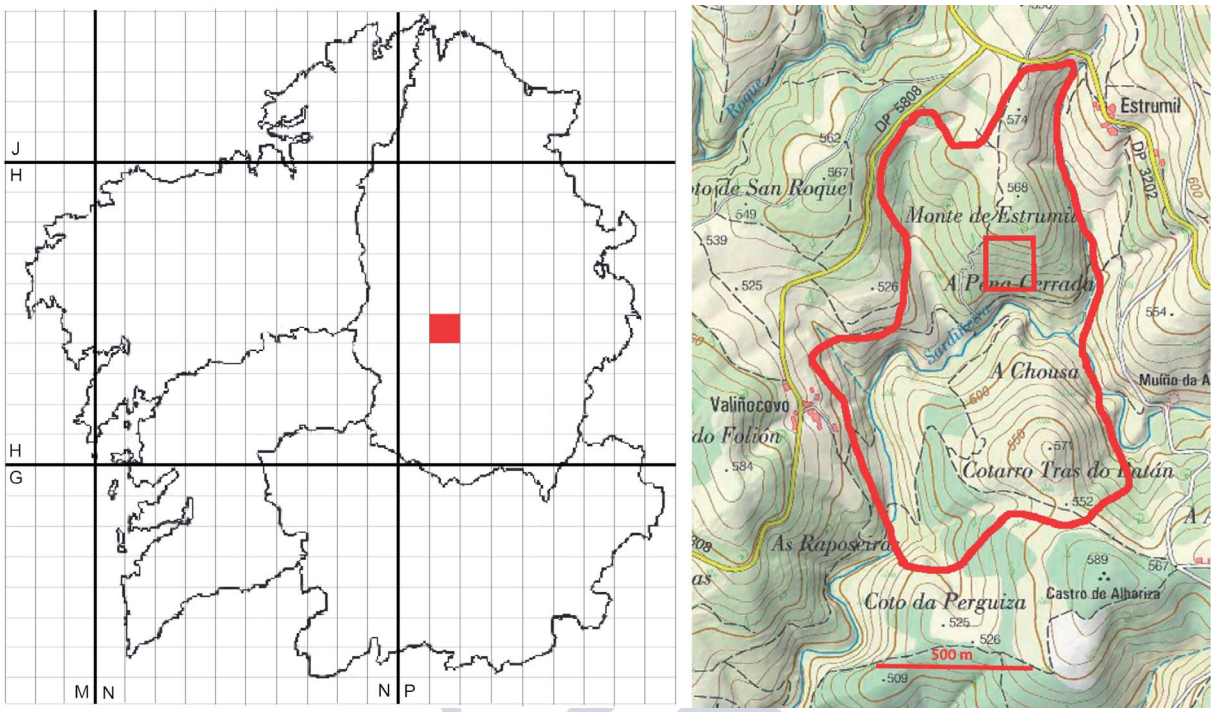

Figure 5.2: Location of the Saviñao experimental field (red square) in the 10x10 km UTM grid map of Galicia (left) and within the perimeter of the burnt area delimited in the topographic map (right).

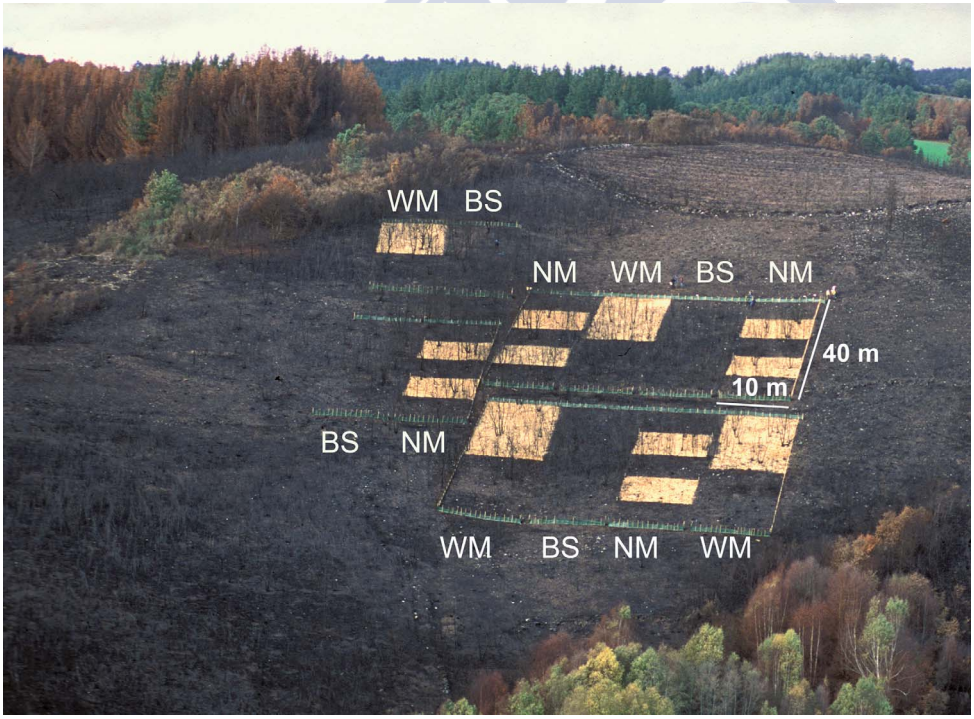

Figure 5.3: Plot distribution in the Saviñao study area. Key: BS, control burnt plots; WM, wide-mulched burnt plots; NM, narrow-mulched burnt plots.

5.3.2 Sampling and chemical analyses of soils, ashes and sediments

One month after the fire but prior to treatment application, ash samples (ashes and charred plant and litter debris, hereafter referred to as "ashes") and soil samples (0-2.5 cm depth) were collected from four of the corridors between plots (not within the plots to prevent trampling on them). The central corridor in each of the four blocks of plots (see Fig. 5.3) was selected and 10 squares of 15x15 cm per corridor were sampled for ashes and combined in a composite sample per corridor, weighed, homogenized and air dried; the same was done for soil. Once the treatments were applied, in each plot and at each sampling date (3, 6, 9 and 12 months after treatment application) soil samples were collected from 10 uniformly distributed sampling squares. These 10 subsamples were combined to yield one composite sample per plot and sampling date. In plots with mulching, samples were taken separately in the area with straw (NM-1 and WM-1) and without straw (NM-0 and WM-0). We did not find straw on the NM-0 and WM-0 areas, nor in the sediments collectors, in any of the samplings. All soil samples were sieved (2 mm) and homogenised in the laboratory, then they were divided into: a) fresh subsamples, which were kept at 4 ℃ for inorganic N measurements; and b) air-dried subsamples for the other analyses. After each sediment-producing rain event (December 2012, February 2013, March 2013, April 2013, June 2013 and November 2013), eroded sediments were collected from the geotextile, homogenized and weighed in situ and aliquots of each plot were transported to the laboratory, where they were air-dried for further analyses.

The dry matter content of soils and sediments was assessed by oven-drying sub-samples at 105 ℃ for 5 h. Due to the wide differences in water holding capacities of soils, sediments and ashes, different sample:solution ratios were used to obtain the "solid suspension" needed for pH measurements, as well as a volume of extract large enough for inorganic N analyses. Soil pH was measured with a pH meter (Metröhm, Switzerland) in water and 1 M KCl employing the standard soil:solution ratio of 1:2.5, while for sediments and ashes a sample:solution ratio of 1:6 was used. For total N and δ^{15}N determination, aliquots of air-dried soils, sediments and ashes were finely ground (<100 μm) in a planetary ball mill (Retsch PM100, Retsch GmbH, Haan, Germany) and then combusted with an elemental analyser (Carlo Erba, Milano, Italy) coupled on-line with an isotopic ratio mass spectrometer (Finnigan Mat, delta C, Bremen, Germany). An elemental reference material (Soil 3 from Eurovector, Milano, Italy) and isotopic standards (IAEA-N1 and IAEA-N2, alternately, from the International Atomic Energy Agency, Vienna, Austria) were included in each set of 10 samples to check the accuracy of the results; if necessary, drift correction was made against internal standards during the run. Inorganic N was extracted by shaking 20 g of soils and sediments or 5 g of ashes for 1 h with 2 M KCl (1:5 soils and sediments:solution ratio and 1:10 ash:solution ratio). Extracts were passed through glass microfibre filters (Whatman GF/A, 125 mm diameter). For NH_4^+-N and NO_3^--N analysis, an extraction-diffusion method described in Fernández-Fernández et al. (2015) was used. For extractable element analyses, soil, sediment and ash samples were shaken for 2 hours with a solution of NH_4Ac 1 M and DTPA 0.005 M (sample:solution ratio 1:5). The extracts and

the corresponding blanks were then filtered through cellulose paper (Filter-Laboratory 1242, 90-mm diameter) and analysed by simultaneous inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista Pro, Mulgrave, Australia) to quantify Al, Ca, Cu, Fe, K, Mg, Mn, Mo, Na, P and Zn concentrations. A calibration curve prepared with certified standards of all elements was measured beforehand and one of the calibration solutions was routinely included in each set of 30 samples as a quality control and, when necessary, the calibration curve was measured again. Analytical-grade chemicals and type I water (ASTM, 2008) were used for analyses.

To ensure the reproducibility and traceability of the results, certified standards were included in each batch of samples and all analyses were carried out in duplicate, being the mean of both measurements used in the statistical procedures (after doing a third analysis if the coefficient of variation was higher than 5%).

5.3.3 Statistical analyses

The working hypothesis of no effects of straw addition on soil properties was tested by means of two sets of one-way ANOVAs: a) straw addition does not modify soil properties in situ (one-way ANOVAs including BS, WM-1 and NM-1 subplots); and b) straw addition does not affect soil properties of the adjacent bare subplots (one-way ANOVAs including BS, WM-0 and NM-0). These two ANOVAs were done for each sampling date and t=0 values were not included as no treatments were applied yet. Similarly, the hypothesis of no effects of straw addition on sediment composition regardless sampling date was tested by one-way ANOVAs comparing the sediments retrieved in BS, WM and NM plots. Moreover, sediments of each erosion event were compared with soils (t=0) and ashes as reference values (one-way ANOVA and Dunnett's test) because they are the likeliest sources of sediments. Curvilinear regression models were also developed to check trends on sediment composition throughout the study period. The effectiveness of mulching dose on erosion rates and nutrient losses was assessed by comparing the accumulated mass of sediments and of each nutrient in BS, WM and NM plots with one-way ANOVAs. For all performed ANOVAs, significant differences among the group means were established at $p<0.05$ (using Tukey's or Dunnett's test) after checking the normal distribution of variables (Shapiro-Wilk's W test) and the equality of variances among treatment groups (Levene's test). A Principal Component Analysis (PCA, based on the correlation matrix, to extract the factors, plus Varimax rotation with Kaiser normalisation) was performed to assess the relationships among the studied variables and whether samples are grouped together according to treatment or sampling date. The anti-image correlation matrix (comprising the negative values of the partial correlation coefficients) was analyzed to detect soil variables less suitable for the factor analysis (Cu and Mo in soils; ^{15}N and Fe in sediments). After this procedure, the Kaiser-Meyer-Olkin measure of sampling adequacy increased from 0.730 to 0.784 (soils) and from 0.742 to 0.795 (sediments), and the Barlett's test of sphericity was highly significant ($p<0.0005$). All statistical analyses were performed with SPSS 15.0 software (SPSS Inc., Chicago, IL).

5.4 Results

The one-way ANOVA checking the effect of straw mulch on soils (Table 5.1) yielded significant differences among treatments only for NH_4^+-N_{soil} (BS > WM-1 = NM-1) and NO_3^--N_{soil} (BS ≥ WM-1 ≥ NM-1) at t=6, $\delta^{15}N_{soil}$ at t=9 (WM-1 ≥ BS ≥ NM-1) and Ca_{soil} (WM-1 ≥ NM-1 ≥ BS) and Mg_{soil} (WM-1 > NM-1 = BS) at t=12 months. When checking the effect of straw on adjacent unmulched soils (Table 5.1), there were small but significant differences for Ca_{soil} at t=3 (WM-0 ≥ BS ≥ NM-0) and Fe_{soil} (NM-0 ≥ BS ≥ WM-0) and K_{soil} (WM-0 ≥ NM-0 ≥ BS) at t=6 months. Most of the studied variables oscillated with time after the fire, although the initial values were higher than the final ones except for Na_{soil} (Table 5.2).

Table 5.1: Statistics of ANOVA-1 to check: A) the effect of mulch (WM-1 and NM-1 vs BS) on pH_{KCl}, $\delta^{15}N$ and concentrations of main nutrients and trace elements in soils from each sampling time after the fire (3, 6, 9 and 12 months); and B) the effect of mulching on the downslope unmulched areas (WM-0 and NM-0 vs BS). Key: BS, control burnt plots; WM-0, wide-mulched burnt plots, section without straw; WM-1, wide-mulched burnt plots, section with straw; NM-0, narrow-mulched burnt plots, section without straw; NM-1, narrow-mulched burnt plots, section with straw. Significant differences are highlighted in bold.

	A) WM-1 and NM-1 vs BS								**B) WM-0 and NM-0 vs BS**							
	3 months		6 months		9 months		12 months		3 months		6 months		9 months		12 months	
	F	Sig.	F	Sig.	F	Sig.	F	Sig.	F	Sig.	F	Sig.	F	Sig.	F	Sig.
pH_{KCl}	0.311	0.741	0.159	0.855	0.059	0.943	2.425	0.144	0.039	0.962	0.797	0.480	0.068	0.935	0.031	0.969
Total N	0.135	0.876	0.673	0.537	0.492	0.627	0.622	0.558	0.297	0.750	0.006	0.994	0.426	0.666	0.380	0.694
$\delta^{15}N$	0.529	0.606	0.384	0.692	4.422	**0.046**	0.536	0.603	0.608	0.565	0.797	0.484	3.034	0.098	0.900	0.440
NH_4-N	0.299	0.749	6.015	**0.022**	1.812	0.218	0.403	0.680	0.042	0.959	2.017	0.189	0.241	0.790	0.081	0.923
NO_3-N	1.439	0.287	5.371	**0.029**	1.907	0.204	0.834	0.465	1.261	0.329	1.539	0.266	0.536	0.603	1.917	0.203
Al	0.132	0.878	0.285	0.759	0.701	0.521	0.528	0.607	0.186	0.833	0.332	0.726	1.002	0.405	0.601	0.569
Ca	1.796	0.227	0.686	0.528	0.299	0.748	4.815	**0.038**	5.803	**0.024**	0.493	0.627	0.054	0.948	1.201	0.345
Cu	0.689	0.527	1.409	0.293	0.897	0.442	0.619	0.560	1.688	0.239	0.822	0.470	0.465	0.642	0.209	0.816
Fe	0.742	0.503	0.035	0.966	0.141	0.870	1.722	0.233	0.071	0.932	8.126	**0.012**	0.082	0.922	0.170	0.846
K	1.054	0.388	0.415	0.672	1.393	0.297	1.751	0.228	1.335	0.311	4.346	**0.048**	0.807	0.479	1.912	0.203
Mg	0.017	0.983	0.052	0.949	0.601	0.569	10.456	**0.006**	0.316	0.737	0.119	0.889	0.216	0.810	1.870	0.209
Mn	2.525	0.141	2.426	0.150	0.312	0.741	2.640	0.132	1.209	0.348	1.177	0.356	0.288	0.757	2.113	0.183
Mo	0.043	0.958	0.168	0.848	1.009	0.402	0.413	0.674	1.067	0.384	0.336	0.723	3.703	0.067	0.720	0.513
Na	4.136	0.053	0.948	0.423	0.441	0.658	1.591	0.256	2.002	0.191	0.463	0.643	0.042	0.959	0.276	0.765
P	0.788	0.484	1.190	0.348	1.629	0.249	0.093	0.912	0.075	0.929	1.073	0.382	0.951	0.426	0.484	0.632
Zn	0.425	0.666	0.099	0.907	0.706	0.519	0.606	0.566	0.794	0.481	0.752	0.499	0.600	0.570	0.406	0.678

Degrees of freedom: among groups, 2; between groups, 9.

Table 5.2: Mean values ± S.D. of pH_{KCl}, $\delta^{15}N$ and concentrations of main nutrients and trace elements in soils for the different treatments and sampling times after the fire. Key: BS, control burnt plots; WM-0, wide-mulched burnt plots, section without straw; WM-1, wide-mulched burnt plots, section with straw; NM-0, narrow-mulched burnt plots, section without straw; NM-1, narrow-mulched burnt plots, section with straw.

Time (months)	**Plots**	**pH_{KCL}**	**Total N** (g kg^{-1})	**^{15}N** (‰)	**$NH_4^+ - N$** (m kg^{-1})	**$NO_3^- - N$** (m kg^{-1})	**Al** (m kg^{-1})	**Ca** (m kg^{-1})	**Cu** (m kg^{-1})	**Fe** (m kg^{-1})	**K** (m kg^{-1})	**Mg** (m kg^{-1})	**Mn** (m kg^{-1})	**Mo** (m kg^{-1})	**Na** (m kg^{-1})	**P** (m kg^{-1})	**Zn** (m kg^{-1})
	BS	3.9 ± 0.1	10.4 ± 0.7	2.0 ± 0.1	98 ± 20	19.2 ± 6.8	570 ± 4	343 ± 13	2.4 ± 0.2	364 ± 28	150 ± 6	77 ± 10	33 ± 3	1.4 ± 0.1	45 ± 4	15 ± 2	6.0 ± 0.5
	WM-0	3.9 ± 0.1	11.0 ± 0.3	1.8 ± 0.2	103 ± 13	16.4 ± 5.3	555 ± 22	391 ± 5	2.4 ± 0.3	355 ± 38	166 ± 8	82 ± 6	38 ± 5	1.4 ± 0.1	55 ± 5	15 ± 3	7.2 ± 0.9
3	WM-1	4.0 ± 0.2	10.8 ± 0.5	1.9 ± 0.2	90 ± 12	13.8 ± 3.0	568 ± 18	430 ± 101	2.6 ± 0.2	324 ± 24	180 ± 19	75 ± 14	46 ± 10	1.4 ± 0.1	56 ± 4	17 ± 1	6.7 ± 0.9
	NM-0	3.9 ± 0.1	10.6 ± 0.4	1.8 ± 0.1	105 ± 18	7.9 ± 3.0	563 ± 20	324 ± 21	3.0 ± 0.3	372 ± 34	151 ± 8	74 ± 4	48 ± 19	1.4 ± 0.1	50 ± 2	16 ± 2	6.4 ± 0.5
	NM-1	3.8 ± 0.1	10.7 ± 0.1	1.8 ± 0.1	81 ± 14	8.0 ± 3.2	559 ± 22	282 ± 16	2.7 ± 0.1	386 ± 53	170 ± 16	74 ± 9	40 ± 16	1.4 ± 0.1	46 ± 1	16 ± 2	6.7 ± 0.5
	BS	3.4 ± 0.1	10.0 ± 0.9	2.1 ± 0.1	66 ± 12	11.1 ± 3.7	538 ± 7	253 ± 27	2.3 ± 0.1	330 ± 14	103 ± 11	49 ± 7	19 ± 2	1.4 ± 0.1	27 ± 4	12 ± 1	4.6 ± 0.5
	WM-0	3.5 ± 0.1	10.0 ± 0.7	2.0 ± 0.2	93 ± 8	12.9 ± 2.3	566 ± 37	284 ± 52	2.5 ± 0.3	294 ± 17	134 ± 4	53 ± 6	24 ± 5	1.4 ± 0.1	31 ± 3	11 ± 1	5.2 ± 0.2
6	WM-1	3.4 ± 0.1	9.5 ± 0.5	2.0 ± 0.2	32 ± 8	2.4 ± 0.9	564 ± 26	276 ± 41	2.7 ± 0.2	321 ± 47	97 ± 3	47 ± 5	27 ± 6	1.4 ± 0.1	23 ± 2	14 ± 1	4.6 ± 0.2
	NM-0	3.4 ± 0.1	10.1 ± 0.3	2.1 ± 0.3	59 ± 17	6.1 ± 2.2	541 ± 26	231 ± 31	2.7 ± 0.2	336 ± 45	110 ± 8	53 ± 6	29 ± 13	1.3 ± 0.1	28 ± 3	12 ± 1	5.0 ± 0.5
	NM-1	3.4 ± 0.1	9.8 ± 0.3	2.2 ± 0.1	29 ± 2	2.0 ± 0.4	551 ± 33	227 ± 14	2.6 ± 0.2	337 ± 55	105 ± 2	49 ± 3	22 ± 8	1.3 ± 0.1	27 ± 1	13 ± 1	4.8 ± 0.5
	BS	3.5 ± 0.1	9.8 ± 0.5	1.8 ± 0.1	76 ± 19	12.3 ± 4.5	444 ± 4	240 ± 23	2.2 ± 0.2	343 ± 16	114 ± 4	54 ± 6	30 ± 4	0.9 ± 0.1	71 ± 5	18 ± 2	3.9 ± 0.5
	WM-0	3.5 ± 0.1	10.2 ± 0.2	1.8 ± 0.1	91 ± 18	16.1 ± 3.8	464 ± 11	227 ± 34	2.4 ± 0.1	323 ± 36	125 ± 15	52 ± 3	30 ± 8	1.0 ± 0.1	73 ± 7	20 ± 4	3.7 ± 0.3
9	WM-1	3.5 ± 0.1	9.3 ± 0.5	1.9 ± 0.1	44 ± 14	8.8 ± 3.8	460 ± 15	217 ± 31	2.7 ± 0.3	324 ± 35	112 ± 8	47 ± 8	29 ± 6	0.9 ± 0.1	65 ± 5	22 ± 2	3.8 ± 0.4
	NM-0	3.5 ± 0.1	9.9 ± 0.1	1.5 ± 0.1	74 ± 19	10.0 ± 4.3	449 ± 14	230 ± 27	2.5 ± 0.3	344 ± 58	105 ± 4	57 ± 5	41 ± 18	0.9 ± 0.1	72 ± 4	21 ± 1	4.3 ± 0.3
	NM-1	3.5 ± 0.1	9.9 ± 0.3	1.5 ± 0.1	42 ± 7	3.0 ± 0.8	441 ± 14	241 ± 20	2.6 ± 0.3	357 ± 67	125 ± 6	58 ± 8	42 ± 18	1.0 ± 0.1	77 ± 8	19 ± 1	4.4 ± 0.2
	BS	3.4 ± 0.1	10.1 ± 0.9	1.8 ± 0.1	32 ± 8	5.1 ± 0.9	401 ± 8	232 ± 31	1.4 ± 0.1	301 ± 12	74 ± 7	37 ± 2	20 ± 4	0.1 ± 0.1	60 ± 6	16 ± 1	2.5 ± 0.5
	WM-0	3.4 ± 0.1	10.4 ± 0.6	1.9 ± 0.2	62 ± 26	9.5 ± 3.0	416 ± 9	202 ± 27	1.5 ± 0.1	275 ± 34	81 ± 11	30 ± 2	18 ± 4	0.1 ± 0.1	61 ± 3	14 ± 2	2.3 ± 0.1
12	WM-1	3.6 ± 0.1	11.4 ± 1.1	1.7 ± 0.1	36 ± 12	6.5 ± 2.1	384 ± 17	378 ± 49	1.6 ± 0.2	224 ± 11	93 ± 7	49 ± 9	33 ± 6	0.1 ± 0.1	72 ± 5	16 ± 1	3.1 ± 0.4
	NM-0	3.4 ± 0.1	9.6 ± 0.6	2.1 ± 0.1	54 ± 20	4.9 ± 0.9	414 ± 13	162 ± 36	1.5 ± 0.2	299 ± 49	60 ± 2	29 ± 5	25 ± 16	0.1 ± 0.1	55 ± 7	16 ± 1	2.2 ± 0.2
	NM-1	3.5 ± 0.1	10.3 ± 0.4	1.9 ± 0.1	25 ± 3	4.0 ± 0.4	405 ± 19	273 ± 14	1.6 ± 0.2	297 ± 55	92 ± 10	42 ± 4	27 ± 9	0.1 ± 0.1	69 ± 3	16 ± 1	2.9 ± 0.4

In the PCA for soil samples (Fig. 5.4 and Table 5.3), the first three components jointly explained 70% of the total variance (41%, 19% and 10%, respectively). Soil extractable Mg, K, Zn, Ca, Mn and pH_{KCl} were strongly associated with the positive side of factor 1 ($r > 0.7$). Regarding factor 2, its positive side was mostly defined by Na and P ($r > 0.7$) and its negative side by Al and $\delta^{15}N$ ($r < -0.6$). Inorganic N (both NH_4^+ and NO_3^-) was strongly associated with the positive side of factor 3 ($r > 0.7$). The distribution of soil samples on the plane defined by the first two factors shows a change of the samples with time after fire, whereas there is no difference among plots from different treatments within each sampling date. Samples from t= 3 and t= 6 months are clearly separated from each other, as well as from those collected at t= 9 and t=12 months, although these last two samplings are intermingled.

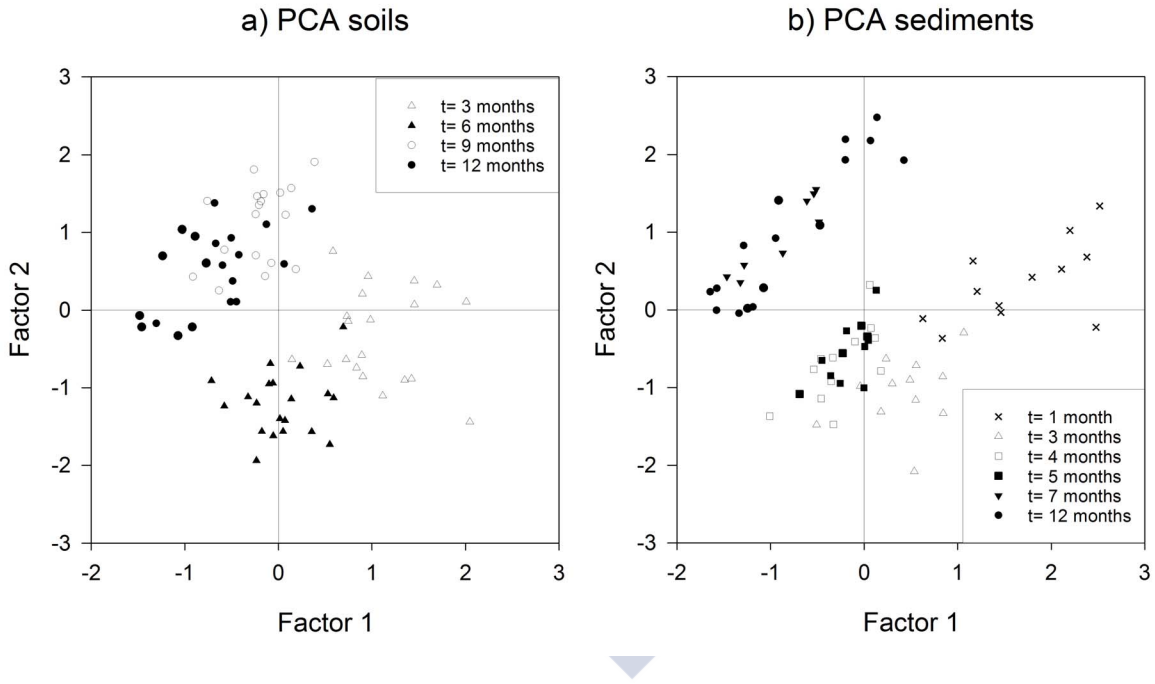

Figure 5.4: Score plots from the principal component analyses (PCAs) performed with soil (a) and sediment (b) data for each treatment and sampling time. Symbols represent different sampling times regardless treatment.

The one-way ANOVAs comparing sediments from BS, WM and NM plots for each sampling date yielded no significant differences among treatments for any of the variables (Table 5.4). Irrespectively of the treatment considered, sediment pH_{KCl}, extractable Ca, Mg, Mn and Zn fitted to curvilinear models with time after treatment application as the independent variable, explaining usually 50-75% of the variance (Figs. 5.5 and 5.6). For the rest of the sediment variables, no suitable regression models were found to explain data variability.

Table 5.3: Matrix of correlations of soil and sediment variables with the first 3 factors (soils) and 2 factors (sediments) obtained by principal component analyses (PCA).

	Soil components			Sediment components	
Variable	1	2	3	1	2
pH_{KCl}	0.767	0.144	0.242	0.912	0.048
Total N	0.529	0.212	0.247	0.674	0.282
$\delta\ ^{15}N$	-0.341	-0.647	0.304		
NH_4^+-N	0.496	-0.125	0.767	0.034	0.732
NO_3^--N	0.122	-0.038	0.922	-0.468	0.240
Al	0.032	-0.678	0.357	-0.147	-0.849
Ca	0.865	0.182	-0.006	0.885	0.296
Cu				0.658	-0.654
Fe	-0.101	-0.055	-0.050		
K	0.914	0.001	0.154	0.566	0.624
Mg	0.931	0.141	0.051	0.905	0.199
Mn	0.768	0.273	0.128	0.821	0.158
Mo				0.741	-0.583
Na	-0.089	0.800	-0.032	0.674	0.477
P	0.233	0.738	0.236	0.089	0.853
Zn	0.871	-0.232	0.220	0.846	-0.134

Table 5.4: Statistics of ANOVA-1 to check the effect of mulch (WM and NM vs BS) on pH_{KCl}, $\delta^{15}N$ and concentrations of main nutrients and trace elements in sediments from each erosion event (1, 3, 4, 5, 7 and 12 months after the fire), as well as for the accumulated mass of nutrients lost by erosion. Key: BS, control burnt plots; WM, wide-mulched burnt plots; NM, narrow-mulched burnt plots.

	Erosion event												Accumulated mass of nutrients	
	1 month		3 months		4 months		5 months		7 months		12 months			
	F	Sig.	F	Sig.	F	Sig.	F	Sig.	F	Sig.	F	Sig.	F	Sig.
pH_{KCl}	0.402	0.681	0.163	0.852	0.348	0.715	0.172	0.845	0.190	0.830	0.032	0.968	----	----
Total N	0.120	0.888	0.442	0.656	0.586	0.576	0.342	0.719	0.254	0.781	0.201	0.822	0.607	0.566
$\delta\ ^{15}N$	0.833	0.466	0.163	0.852	0.722	0.512	0.197	0.825	0.102	0.904	0.268	0.771	----	----
NH_4-N	0.125	0.884	2.236	0.163	1.344	0.309	0.533	0.604	0.212	0.813	0.069	0.934	0.305	0.744
NO_3-N	4.176	0.052	3.461	0.077	2.656	0.124	3.019	0.099	0.459	0.646	0.993	0.408	1.212	0.342
Al	0.927	0.430	0.744	0.502	1.576	0.259	0.880	0.448	0.933	0.428	0.620	0.559	0.359	0.708
Ca	0.860	0.455	0.247	0.786	0.056	0.946	0.058	0.944	1.129	0.365	0.143	0.869	0.377	0.696
Cu	0.585	0.577	1.697	0.237	2.582	0.130	1.613	0.252	2.401	0.146	3.676	0.068	1.289	0.322
Fe	0.597	0.571	0.174	0.843	0.797	0.480	0.661	0.540	1.386	0.299	3.904	0.060	0.114	0.893
K	0.825	0.469	1.773	0.224	1.404	0.295	0.778	0.488	0.073	0.930	1.034	0.394	0.402	0.681
Mg	0.781	0.487	1.110	0.371	0.383	0.693	0.200	0.822	0.246	0.787	0.139	0.872	0.385	0.691
Mn	0.049	0.953	0.105	0.901	0.343	0.719	0.177	0.841	0.064	0.938	0.055	0.947	0.158	0.856
Mo	0.361	0.706	0.171	0.845	0.061	0.941	0.163	0.852	0.402	0.680	0.100	0.906	0.391	0.687
Na	0.236	0.795	0.403	0.680	0.767	0.493	0.493	0.626	0.199	0.823	0.313	0.739	0.603	0.568
P	3.424	0.078	0.549	0.596	0.633	0.553	0.074	0.929	0.124	0.885	0.900	0.440	0.605	0.567
Zn	1.833	0.215	0.624	0.558	1.982	0.193	1.200	0.345	0.719	0.513	0.910	0.436	0.622	0.558

Degrees of freedom: among groups, 2; between groups, 9.

Compared with that of ashes, the pH_{KCl} of the sediments was similar in the first erosion event and lower in those successively eroded (Tables 5.5 and 5.6). Sediments experienced a progressive acidification with time, but their pH_{KCl} was always higher than that of the soil at t=0 (Tables 5.5 and 5.7). Irrespectively of the erosion event, total $N_{sediments}$ and $\delta^{15}N_{sediments}$ were similar to those in ashes but, in most cases, they were higher (total N) or lower ($\delta^{15}N$) than in soil. The concentration of NH_4^+-$N_{sediments}$ (except for those collected at t= 3 months) was well over the ash and soil levels, while almost no differences between sediments, ashes and soils were found for NO_3^- -N. Levels of K and Na in sediments were similar or lower than in ashes, but always higher than in soil. Extractable $Ca_{sediments}$ and $Mg_{sediments}$ were lower that Ca_{ashes} and Mg_{ashes} in the first erosion event, but similar in the subsequent events, and much higher than Ca_{soil} and Mg_{soil}. In almost all cases, extractable $Al_{sediments}$ and $Fe_{sediments}$ were higher than in ashes and lower than in soil. Depending on the erosion event considered, sediments showed Mn levels lower or similar to ashes, and higher or similar to soil. If ashes and soil values are taken as a reference, $Zn_{sediments}$ levels were higher in the first 3-4 erosion events and similar in the rest, while Cu levels were lower in the two last erosion events and similar in the previous ones. Finally, the extractable Mo levels in sediments were similar or lower than in ashes but always higher than in soil, whereas $P_{sediments}$ was lower than P_{ashes} except in the last two erosion events but similar to P_{soils} in most cases.

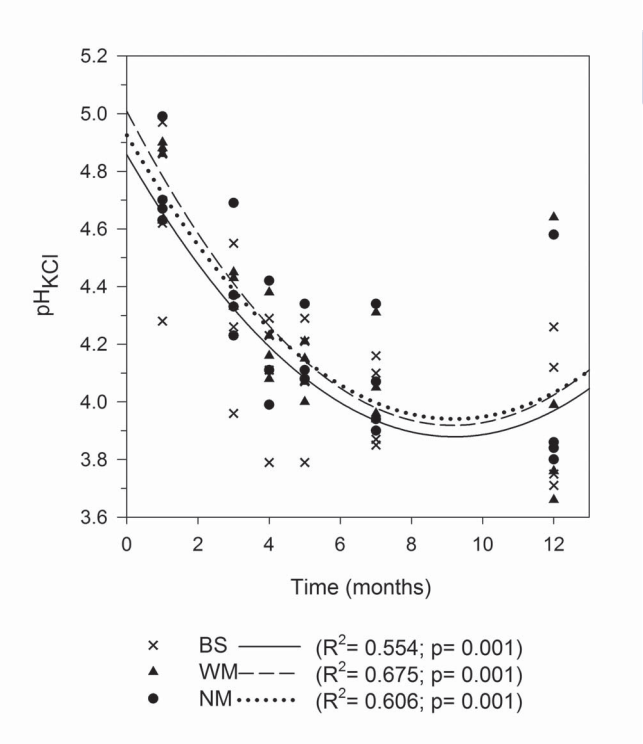

Figure 5.5: Significant curvilinear regression models for sediment pH_{KCl} with time after the fire as independent variable. Key: BS, control burnt plots; WM, wide-mulched burnt plots; NM, narrow-mulched burnt plots.

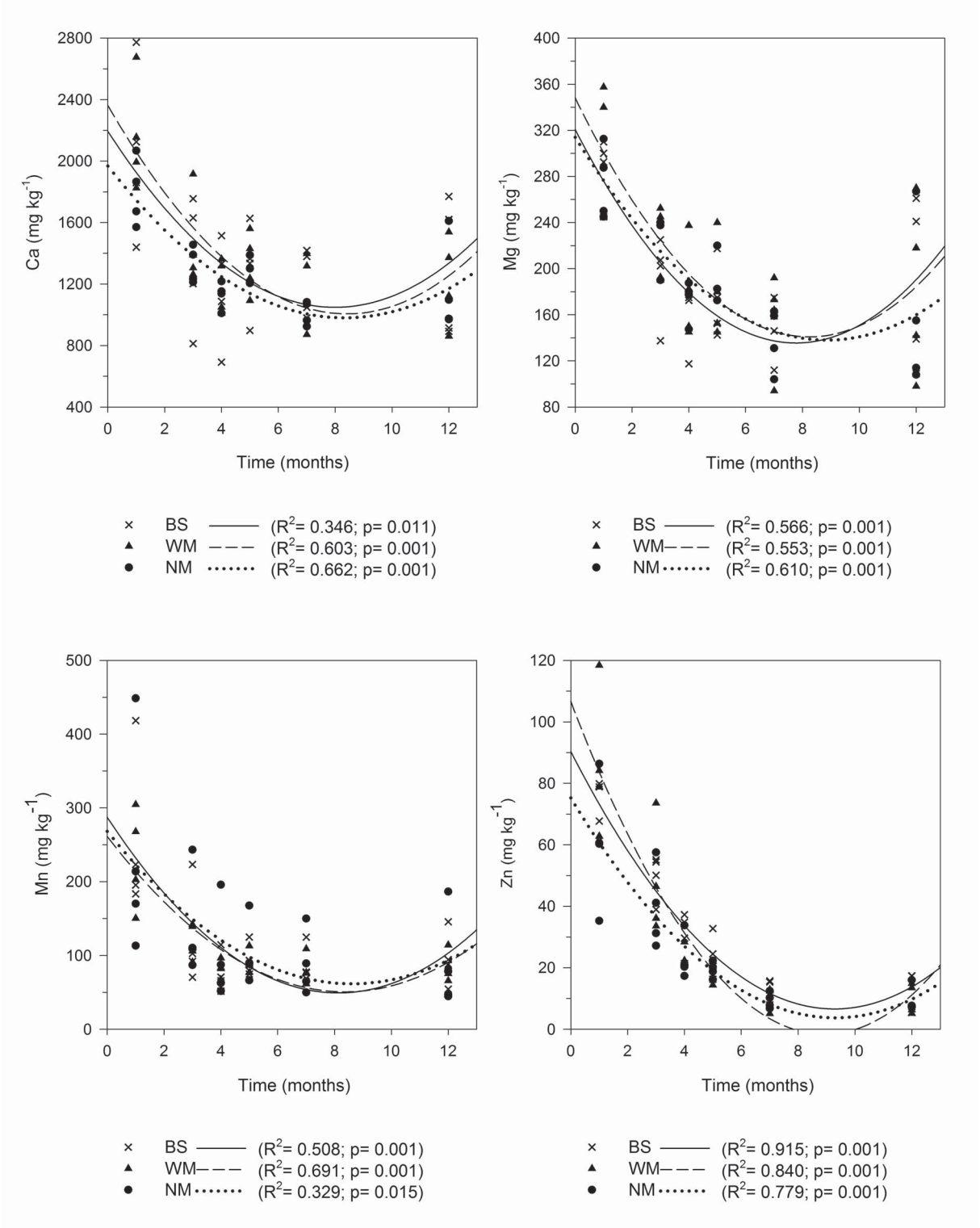

Figure 5.6: Significant curvilinear regression models for sediment Ca, Mg, Mn and Zn with time after the fire as independent variable. Key: BS, control burnt plots; WM, wide-mulched burnt plots; NM, narrow-mulched burnt plots.

Table 5.5: Mean values ± S.D. of pH_{KCl}, $\delta^{15}N$ and concentrations of main nutrients and trace elements in sediments for the different plots and erosion events. Key: BS, control burnt plots; WM, wide-mulched burnt plots; NM, narrow-mulched burnt plots. For comparison purposes, soil (t=0) and ash values are also provided.

Time (months)	**Plots**	**pH_{KCL}**	**Total N** (g kg^{-1})	**^{15}N** (‰)	**$NH_4^+ - N$** (m kg^{-1})	**$NO_3^- - N$** (m kg^{-1})	**Al** (m kg^{-1})	**Ca** (m kg^{-1})	**Cu** (m kg^{-1})	**Fe** (m kg^{-1})	**K** (m kg^{-1})	**Mg** (m kg^{-1})	**Mn** (m kg^{-1})	**Mo** (m kg^{-1})	**Na** (m kg^{-1})	**P** (m kg^{-1})	**Zn** (m kg^{-1})
1	BS	4.7 ± 0.2	26.7 ± 2.6	0.5 ± 0.1	233 ± 24	10.5 ± 1.9	153 ± 18	2049 ± 279	2.8 ± 0.3	129 ± 15	442 ± 25	287 ± 14	255 ± 55	2.6 ± 0.2	88 ± 13	19 ± 2	72 ± 4
	WM	4.8 ± 0.1	27.8 ± 3.8	0.1 ± 0.3	222 ± 23	6.1 ± 1.0	131 ± 19	2162 ± 184	3.0 ± 0.2	110 ± 12	491 ± 56	308 ± 25	231 ± 34	3.0 ± 0.3	94 ± 11	21 ± 3	86 ± 12
	NM	4.7 ± 0.1	25.6 ± 3.0	0.6 ± 0.3	238 ± 24	5.3 ± 1.0	162 ± 12	1794 ± 110	3.2 ± 0.3	122 ± 9	429 ± 12	274 ± 16	236 ± 74	2.8 ± 0.4	84 ± 3	13 ± 1	61 ± 10
3	BS	4.3 ± 0.1	18.3 ± 1.7	0.9 ± 0.1	74 ± 6	3.9 ± 0.5	222 ± 15	1350 ± 215	2.5 ± 0.2	184 ± 11	212 ± 23	193 ± 19	122 ± 34	2.2 ± 0.1	68 ± 7	11 ± 0	50 ± 4
	WM	4.4 ± 0.1	21.3 ± 3.4	0.7 ± 0.3	79 ± 4	2.6 ± 0.2	233 ± 30	1468 ± 151	3.0 ± 0.2	188 ± 13	258 ± 31	220 ± 17	120 ± 13	2.3 ± 0.1	75 ± 6	12 ± 1	47 ± 9
	NM	4.4 ± 0.1	19.8 ± 1.0	0.9 ± 0.2	89 ± 5	2.5 ± 0.4	293 ± 69	1323 ± 59	3.5 ± 0.6	210 ± 55	282 ± 26	226 ± 12	137 ± 36	2.2 ± 0.2	73 ± 4	11 ± 1	39 ± 7
4	BS	4.1 ± 0.1	17.3 ± 2.4	0.7 ± 0.1	189 ± 22	10.2 ± 0.5	214 ± 12	1156 ± 178	2.5 ± 0.2	166 ± 9	205 ± 20	160 ± 14	76 ± 14	2.1 ± 0.1	50 ± 8	13 ± 1	31 ± 4
	WM	4.2 ± 0.1	20.2 ± 3.9	0.6 ± 0.3	224 ± 16	10.6 ± 1.3	226 ± 32	1185 ± 90	2.4 ± 0.1	147 ± 9	250 ± 26	179 ± 21	82 ± 6	2.1 ± 0.1	62 ± 8	14 ± 2	24 ± 2
	NM	4.2 ± 0.1	15.9 ± 1.8	1.0 ± 0.2	193 ± 9	7.4 ± 1.2	269 ± 19	1129 ± 43	3.0 ± 0.3	164 ± 16	237 ± 8	173 ± 9	99 ± 33	2.1 ± 0.1	61 ± 6	11 ± 1	23 ± 4
5	BS	4.1 ± 0.1	24.3 ± 2.1	0.4 ± 0.1	194 ± 14	12.2 ± 1.3	233 ± 20	1306 ± 151	2.4 ± 0.2	161 ± 14	222 ± 20	172 ± 17	93 ± 11	2.1 ± 0.1	49 ± 5	14 ± 1	24 ± 4
	WM	4.1 ± 0.1	25.4 ± 3.9	0.3 ± 0.3	207 ± 9	9.0 ± 1.3	225 ± 26	1330 ± 103	2.3 ± 0.1	143 ± 6	246 ± 18	179 ± 22	91 ± 8	2.1 ± 0.1	54 ± 5	14 ± 1	19 ± 2
	NM	4.2 ± 0.1	22.0 ± 2.5	0.5 ± 0.3	207 ±7	7.8 ± 1.3	265 ± 22	1278 ± 42	2.7 ± 0.2	156 ± 13	247 ± 11	187 ± 11	103 ± 22	2.1 ± 0.1	55 ± 4	13 ± 1	19 ± 1
7	BS	4.0 ± 0.1	17.7 ± 1.6	0.9 ± 0.1	208 ± 7	16.4 ± 6.6	124 ± 17	1207 ± 112	1.0 ± 0.1	121 ± 10	310 ± 30	148 ± 13	87 ± 13	0.2 ± 0.1	60 ± 6	21 ± 4	12 ± 2
	WM	4.1 ± 0.1	16.6 ± 2.0	0.7 ± 0.3	229 ± 13	15.9 ± 6.3	111 ± 11	1165 ± 120	1.0 ± 0.1	100 ± 4	337 ± 68	156 ± 21	81 ± 10	0.2 ± 0.1	64 ± 6	20 ± 4	10 ± 2
	NM	4.1 ± 0.1	16.1 ± 1.2	0.8 ± 0.3	237 ± 54	9.4 ± 4.1	139 ± 14	1010 ± 39	1.3 ± 0.1	108 ± 12	321 ± 44	139 ± 14	88 ± 22	0.2 ± 0.1	59 ± 2	18 ± 3	9 ± 1
12	BS	4.0 ± 0.1	19.4 ± 2.4	1.3 ± 0.1	288 ± 43	21.2 ± 5.0	158 ± 33	1300 ± 230	1.2 ± 0.1	203 ± 17	400 ± 71	188 ± 37	96 ± 19	0.2 ± 0.1	83 ± 17	23 ± 4	14 ± 3
	WM	4.0 ± 0.2	19.7 ± 2.1	1.1 ± 0.3	259 ± 78	52.8 ± 24.8	151 ± 50	1224 ± 148	1.2 ± 0.1	153 ± 16	315 ± 52	182 ± 38	85 ± 10	0.2 ± 0.1	69 ± 9	20 ± 3	10 ± 2
	NM	4.0 ± 0.2	18.0 ± 1.5	1.3 ± 0.3	290 ± 73	34.0 ± 11.1	205 ± 22	1163 ± 152	1.7 ± 0.2	202 ± 9	284 ± 52	161 ± 37	89 ± 33	0.1 ± 0.1	71 ± 12	18 ± 2	10 ± 2
Ashes	Mean	4.8 ± 0.1	17.9 ± 0.5	1.2 ± 0.1	145 ± 15	3.9 ± 2.4	64 ± 6	1150 ± 95	2.6 ± 0.2	54 ± 11	351 ± 12	172 ± 11	146 ± 11	1.9 ± 0.2	86 ± 5	28 ± 1	12 ± 1
Soil ($t = 0$)	Mean	3.3 ± 0.1	10.7 ± 0.8	2.6 ± 0.4	110 ± 27	11.2 ± 10.4	540 ± 23	282 ± 89	2.4 ± 0.2	292 ± 70	121 ± 17	46 ± 16	37 ± 28	1.6 ± 0.2	35 ± 3	13 ± 2	6 ± 1

In the PCA for sediment samples (Fig. 5.4 and Table 5.3), the first two components jointly explained 71% of the variance (46% and 25%, respectively). The variables most strongly correlated with the positive side of factor 1 were pH_{KCl}, Mg, Ca, Zn, Mn and Mo ($r > 0.7$), whereas P and NH_4^+ were strongly associated ($r > 0.7$) with the positive side of factor 2 and Al and Cu with the negative one ($r < -0.7$). The distribution of sediment samples on the plane defined by the first two factors showed a change with time after fire and lack of differences among treatments within each sampling date. Sediments from t= 1 month are well separated from all the other erosion events, samples from t= 3 are slightly apart from the preceding (t= 1 month) and the two subsequent events (t= 4 and 5 months), the latter being intermingled. Sediments from t=7 and 12 months are close together and further away from the others.

During the first year after the wildfire, less than 500 kg ha^{-1} of sediments were eroded, being the losses of elements lowest for NO_3^--N, Cu, Mo, P and Zn (< 10 g ha^{-1}), intermediate for NH_4^+-N, Al, Fe, K, Mg, Mn and Na (20-100 g ha^{-1}) and highest for Ca (around 400 g ha^{-1}) and total N (5 kg ha^{-1}) (Table 5.8). While NO_3^--N, Al, Fe and Zn losses accounted for around 10% of the corresponding ash extractable elements, the percentage of the other elements accounted for 5% (total N, NH_4^+-N, Ca and Mg) or less (Cu, K, Mn, Mo, Na and P) (Table 5.8). If extractable nutrients in ash+topsoil were taken as a reference, the nutrient losses in eroded sediments never exceeded 0.7%, having Al and Fe the lowest losses (0.04 and 0.06% respectively) (Table 5.8). According to the one-way ANOVA, neither the total mass of sediments nor the mass of any nutrient lost by erosion was affected by the tested treatments (Table 5.4).

Table 5.6: Statistics of ANOVA-1 to compare the main properties of sediments from each erosion event with those of ashes (Dunnett's test). Only significant differences are shown, in bold when sediments > ashes and in regular type when sediments < ashes. Key: BS, control burnt plots; WM, wide-mulched burnt plots; NM, narrow-mulched burnt plots.

		sed. 1 month		sed. 3 months		sed. 4 months		sed. 5 months		sed. 7 months		sed. 12 months	
		F	sig.	F	sig.	F	sig.	F	sig.	F		F	sig.
	BS				0.010		0.000		0.000		0.000		0.008
pH_{KCl}	WM	0.42		5.40	0.023	14.10	0.001	20.06	0.000	20.33	0.000	6.26	0.012
	NM				0.026		0.001		0.000		0.000		0.013
	BS												
Total N	WM	2.65		0.61		0.51		1.70		0.35		0.28	
	NM												
	BS												
$\delta^{15}N$	WM	3.69	0.018	0.87		1.49		3.54	0.030	0.75		0.31	
	NM												
	BS		**0.041**		0.001				**0.046**				
NH_4-N	WM	3.81		11.32	0.001	3.78	**0.015**	5.46	**0.012**	1.98		1.38	
	NM		**0.031**		0.004				**0.012**				
	BS		**0.018**				**0.010**		**0.003**				
NO_3-N	WM	3.94		0.82		6.31	**0.006**	6.04		1.37		2.22	
	NM												
	BS		**0.003**		**0.033**		**0.000**		**0.000**		**0.011**		
Al	WM	9.38	**0.017**	6.48	**0.023**	20.46	**0.000**	20.47	**0.000**	7.13	**0.043**	3.37	
	NM		**0.001**		**0.003**		**0.000**		**0.000**		**0.003**		**0.023**
	BS		**0.015**										
Ca	WM	5.67	**0.007**	0.74		0.03		0.46		0.59		0.16	
	NM												
	BS										0.000		0.000
Cu	WM	1.03		1.77		2.16		1.59		62.92	0.000	23.89	0.000
	NM										0.000		0.001
	BS		**0.001**		**0.021**		**0.000**		**0.000**		**0.000**		**0.000**
Fe	WM	9.93	**0.008**	5.98	**0.018**	24.66	**0.000**	23.22	**0.000**	11.67	**0.007**	29.43	**0.000**
	NM		**0.002**		**0.007**		**0.000**		**0.000**		**0.002**		**0.000**
	BS				0.008		0.001		0.001				
K	WM	3.00	**0.031**	4.84		9.22	0.013	9.01	0.006	0.16		0.90	
	NM						0.006		0.006				
	BS		**0.006**										
Mg	WM	8.38	**0.002**	1.77		0.18		0.14		0.53		0.11	
	NM		**0.013**										
	BS								0.058		0.041		
Mn	WM	0.97		0.23		2.76		3.17	0.050	4.13	0.025	1.86	
	NM										0.047		
	BS										0.000		0.000
Mo	WM	3.07	**0.038**	1.61		1.73		1.68		174.84	0.000	172.11	0.000
	NM										0.000		0.000
	BS						0.007		0.000		0.008		
Na	WM	0.23		1.96		5.17	0.064	14.50	0.001	6.65	0.019	0.53	
	NM						0.050		0.001		0.006		
	BS		0.032		0.000		0.000		0.000				
P	WM	7.64		42.63	0.000	22.92	0.000	25.28	0.000	1.37		2.31	
	NM		0.001		0.000		0.000		0.000				
	BS		**0.001**		**0.002**		**0.001**		**0.007**				
Zn	WM	15.44	**0.000**	8.24	**0.004**	8.00	**0.030**	4.81		0.85		0.80	
	NM		**0.003**		**0.020**		**0.037**		**0.084**				

Degrees of freedom: among groups. 3; between groups. 12.

Table 5.7: Statistics of ANOVA-1 to compare the main properties of sediments from each erosion event with those of burnt soil just after the fire (Dunnett's test). Only significant differences are shown, in bold when sediments > soil and in regular type when sediments < soil. Key: BS, control burnt plots; WM, wide-mulched burnt plots; NM, narrow-mulched burnt plots.

		sed. 1 month		sed. 3 months		sed. 4 months		sed. 5 months		sed. 7 months		sed. 12 months	
		F	sig.	F	sig.	F	sig.	F	sig.	F		F	sig.
	BS		**0.001**		**0.001**		**0.001**		**0.001**		**0.001**		**0.041**
pH $_{KCl}$	WM	54.98	**0.001**	33.17	**0.001**	25.21	**0.001**	29.73	**0.001**	19.41	**0.001**	4.39	**0.028**
	NM		**0.001**		**0.001**		**0.001**		**0.001**		**0.001**		**0.025**
	BS		**0.004**		**0.047**				**0.007**		**0.012**		**0.012**
Total N	WM	8.53	**0.002**	5.67	**0.007**	2.56	**0.048**	7.10	**0.004**	4.80	**0.034**	5.73	**0.010**
	NM		**0.006**		**0.018**				**0.021**		**0.049**		**0.033**
	BS		0.001		0.001		0.001		0.001		0.001		0.008
δ ^{15}N	WM	21.55	0.001	17.48	0.001	15.76	0.001	24.02	0.001	13.92	0.001	7.88	0.002
	NM		0.001		0.001		0.001		0.001		0.001		0.008
	BS		**0.005**		0.021		**0.011**		**0.001**				
NH_4-N	WM	7.94	**0.009**	3.96	0.045	9.46	**0.001**	16.96	**0.001**	4.07	**0.034**	2.18	
	NM		**0.003**				**0.008**		**0.001**		**0.024**		
	BS												
NO_3-N	WM	1.11		2.54		0.38		0.51		0.38		1.63	
	NM												
	BS		0.001		0.001		0.001		0.001		0.001		0.001
Al	WM	159.27	0.001	14.72	0.001	56.20	0.001	52.91	0.001	242.33	0.001	32.87	0.001
	NM		0.001		0.002		0.001		0.001		0.001		0.001
	BS		**0.001**		**0.001**		**0.001**		**0.001**		**0.001**		**0.002**
Ca	WM	24.26	**0.001**	16.39	**0.001**	17.61	**0.001**	28.07	**0.001**	24.37	**0.001**	9.08	**0.003**
	NM		**0.001**		**0.001**		**0.001**		**0.001**		**0.001**		**0.005**
	BS										0.001		0.001
Cu	WM	2.14		2.37		2.75		1.44		44.87	0.001	16.45	0.001
	NM										0.001		0.012
	BS		0.001				0.002		0.002		0.001		0.031
Fe	WM	18.07	0.001	2.24		10.94	0.001	12.05	0.001	22.83	0.001	7.30	0.002
	NM		0.001				0.002		0.001		0.001		0.030
	BS		**0.001**		**0.047**		**0.013**		**0.002**		**0.024**		**0.006**
K	WM	28.95	**0.001**	9.00	**0.004**	11.27	**0.001**	15.13	**0.001**	5.49	**0.011**	5.21	**0.050**
	NM		**0.001**		**0.001**		**0.001**		**0.001**		**0.017**		
	BS		**0.001**		**0.001**		**0.001**		**0.001**		**0.001**		**0.030**
Mg	WM	49.66	**0.001**	32.21	**0.001**	18.72	**0.001**	18.18	**0.001**	11.00	**0.001**	3.89	**0.037**
	NM		**0.001**		**0.001**		**0.001**		**0.001**		**0.003**		
	BS		**0.023**						**0.050**				
Mn	WM	4.27	**0.043**	2.91		1.84		4.08	**0.058**	2.53		1.62	
	NM		**0.038**		**0.050**				**0.021**				
	BS		**0.041**		**0.013**		**0.001**		**0.001**		0.001		0.001
Mo	WM	5.63	**0.007**	7.14	**0.004**	15.35	**0.001**	15.46	**0.001**	158.70	0.001	154.52	0.001
	NM		**0.018**		**0.007**		**0.001**		**0.001**		0.001		0.001
	BS		**0.002**		**0.002**						**0.007**		**0.032**
Na	WM	10.14	**0.001**	12.88	**0.001**	3.67	**0.033**	4.84	**0.020**	7.91	**0.003**	3.17	
	NM		**0.004**		**0.001**		**0.042**		**0.014**		**0.009**		
	BS												**0.049**
P	WM	3.97	**0.041**	1.37		0.54		0.08		1.14		2.61	
	NM												
	BS		**0.001**		**0.001**		**0.001**		**0.001**		**0.033**		**0.050**
Zn	WM	18.61	**0.001**	11.59	**0.001**	15.92	**0.001**	13.69	**0.002**	2.88		2.40	
	NM		**0.001**		**0.005**		**0.002**		**0.002**				

Degrees of freedom: among groups. 3; between groups. 12.

Table 5.8: Accumulated mass of sediments and nutrients lost by erosion (mean values ± S.D.), ash nutrients lost by erosion (%) and ash+topsoil nutrients lost by erosion (%) for the different plots. Key: BS, control burnt plots; WM, wide-mulched burnt plots; NM, narrow-mulched burnt plots.

	Mas of sediments and nutrients lost by erosion			Ash nutrients lost by erosion (%)			Ash+topsoil nutrients lost by erosion (%)		
	BS	WM	NM	BS	WM	NM	BS	WM	NM
Sediments (kg ha^{-1})	347 ± 372	310 ± 172	414 ± 309						
Total N (kg ha_{-1})	4.81 ± 1.09	6.40 ± 1.37	5.81 ± 0.34	3.86	5.13	4.66	0.17	0.23	0.21
NH_4^+-N (g ha_{-1})	44.2 ± 12.3	50.4 ± 11.6	56.0 ± 7.9	4.36	4.98	5.54	0.15	0.18	0.20
NO_3^--N (g ha_{-1})	2.94 ± 1.23	8.94 ± 5.05	3.28 ± 1.05	10.74	32.63	11.97	0.10	0.32	0.12
Extractable Al (g ha_{-1})	45.4 ± 17.1	61.2 ± 20.7	65.0 ± 13.3	10.19	13.71	14.58	0.03	0.05	0.05
Extractable Ca (g ha_{-1})	336 ± 87	430 ± 94	394 ± 36	4.19	5.36	4.92	0.43	0.55	0.50
Extractable Cu (g ha_{-1})	0.48 ± 0.09	0.69 ± 0.17	0.81 ± 0.16	2.64	3.77	4.42	0.08	0.11	0.13
Extractable Fe (g ha_{-1})	39.3 ± 14.6	45.6 ± 13.0	47.7 ± 10.4	10.45	12.10	12.66	0.05	0.06	0.06
Extractable K (g ha_{-1})	71.4 ± 19.7	96.1 ± 26.7	89.8 ± 11.4	2.92	3.92	3.67	0.22	0.29	0.28
Extractable Mg (g ha_{-1})	47.5 ± 13.7	61.9 ± 15.9	59.9 ± 5.8	3.96	5.16	5.00	0.35	0.45	0.44
Extractable Mn (g ha_{-1})	32.5 ± 9.0	37.1 ± 8.7	39.8 ± 10.2	3.19	3.65	3.91	0.31	0.36	0.39
Extractable Mo (g ha_{-1})	0.41 ± 0.11	0.51 ± 0.11	0.52 ± 0.07	3.06	3.84	3.92	0.10	0.13	0.13
Extractable Na (g ha_{-1})	15.3 ± 3.5	21.7 ± 6.2	20.2 ± 1.9	2.56	3.62	3.36	0.16	0.23	0.21
Extractable P (g ha_{-1})	3.57 ± 0.81	4.63 ± 0.89	3.77 ± 0.34	1.86	2.41	1.97	0.10	0.13	0.11
Extractable Zn (g ha_{-1})	8.78 ± 1.38	10.33 ± 0.95	9.19 ± 0.55	10.44	12.28	10.92	0.59	0.70	0.62

5.5 Discussion

Fires lead to an increased soil pH as a result of the oxides and carbonates of basic ions supplied by ashes (Certini, 2005). Although soil alkalinity due to burning might persist during several years (Antos et al., 2003), it is supposed to slowly return to pre-fire values due to leaching of basic ions during the wet season (see references in Couto-Vázquez et al. (2011)). Although we do not have pre-fire values, our results for soil pH seem to agree with other studies in the same region (Couto-Vázquez and González-Prieto, 2006; Gómez-Rey and González-Prieto, 2014), in which soil pH of burnt plots decreased to values similar to unburnt plots within the first year after the fire. Concurrently, there was a significant acidification of sediments with time which can be explained by the loss of soil exchangeable cations by leaching and runoff as reported elsewhere (Gómez-Rey et al., 2013b; Robichaud et al., 2006). As in other experiments testing mulching effectiveness, there was no effect of straw addition on the pH of either soils or sediments (Gómez-Rey et al., 2013a; Gómez-Rey et al., 2013b; Gómez-Rey and González-Prieto, 2014; Robichaud et al., 2006).

Soil and sediment total N concentrations neither showed a clear trend during the study nor were affected by mulching, as also reported Gómez-Rey et al. (2013a) and Gómez-Rey et al. (2013b). As these authors suggest, although N-rich sediments are continuously eroded, these losses are likely not reflected in the successive measurements of soil total N concentration because the big soil N pool masks those losses. Similarly, neither $\delta^{15}N_{soils}$ nor $\delta^{15}N_{sediments}$ showed a trend with time and they were not affected by treatments, although Gómez-Rey et al. (2013a)

and Gómez-Rey et al. (2013b) found that both variables were influenced by time after the fire due to enhanced N outputs (nitrates) depleted in ^{15}N. It seems that in our case N losses through erosion and leaching are not that important to modify ^{15}N, likely due to the four-fold lower annual precipitation in our study area. Sediments and ashes shared similar concentrations of total N, which were 1.5-2 fold higher than soil values, whereas $\delta^{15}N_{sediments}$ and $\delta^{15}N_{ashes}$ were also similar but slightly below soil levels; both patterns agree with the data presented in Gómez-Rey et al. (2013b) and shows that the contribution of ashes to the eroded sediments was higher than that of soil.

The oscillating values of soil NH_4^+-N contrast with the decrease with time recorded in other studies (Gimeno-García et al., 2000; Gómez-Rey et al., 2013a; Gómez-Rey and González-Prieto, 2014), most probably due to differences in erosion rates as the soil NH_4^+-N decrease and the extent of erosion of N-rich ashes and sediments are tightly coupled (Gómez-Rey et al., 2013a; Gómez-Rey et al., 2013b). In sediments the concentration of extractable NH_4^+ was within the same range as in a prescribed burnt area (Gómez-Rey et al., 2013b) and no clear trend with time was found in any case, most probably because the NH_4^+ pool is subjected to simultaneous and counteracting processes. Extractable NH_4^+ in sediments is often abundant right after burning because of the high concentration of extractable NH_4^+ in the ash, but it decreases with time due to ash loss by erosion, translocation and condensation in deeper soil layers, uptake by newly sprouted vegetation, and nitrification (see de Koff et al. (2006) and references therein). In our case, the concentration of NH_4^+ in sediments was higher than in soils and ashes, while Gómez-Rey et al. (2013b) found that NH_4^+ concentrations in sediments were also higher than those of burnt soils, but only half than in ashes. Soil NH_4^+ was not significantly affected by mulching application, as also reported in other studies (Gómez-Rey et al., 2013a; Gómez-Rey and González-Prieto, 2014). For NH_4^+ in sediments we did not record an effect of mulching whereas Gómez-Rey et al. (2013b) found that it reduced sediment NH_4^+ during the second half of the study.

Post-fire increases in soil NO_3^- of different magnitude and timing have been reported (Chandler et al., 1983; Couto-Vázquez and González-Prieto, 2006; Gómez-Rey and González-Prieto, 2014; Prieto-Fernández et al., 1993). Soil NO_3^- concentrations in our experiment were similar to those reported after a wildfire nearby (Gómez-Rey and González-Prieto, 2014) but much lower than in burnt plots after a prescribed fire in the same region (Gómez-Rey et al., 2013a). The concentrations of NO_3^- in the sediments collected throughout the first post-fire year agree with the results of several authors (Gimeno-García et al., 2000; Gómez-Rey et al., 2013b; Robichaud and Brown, 1999; Robichaud et al., 2006), but the concentration of NO_3^- in ashes was rather low (25 times lower than in Gómez-Rey et al. (2013b)) and within the sediment's range instead of well above them. There was no effect of mulching on soil NO_3^- (same as in Gómez-Rey et al. (2013a) and Gómez-Rey and González-Prieto (2014)) and sediment NO_3^- was not affected by straw addition either, although other studies showed lower sediment NO_3^- concentrations in mulched plots (Gómez-Rey et al., 2013b). These results confirm the hypothesis of Gómez-Rey

et al. (2013a) that mulching does not have an effect on net mineralisation and nitrification, as neither NH_4^+ nor NO_3^- concentrations are affected by treatment application.

Soil P concentration was within the same range reported in other studies (Gómez-Rey et al., 2013a; Gómez-Rey and González-Prieto, 2014), but instead of decreasing with time it oscillates during the study period. High post-fire P_{soil} concentrations are a result of the increased mineralisation of organic P (Cade-Menun et al., 2000; Saá et al., 1994) and the higher solubility of inorganic P when pH increases towards neutrality (Certini, 2005). Soil P tends to decrease afterwards due to sediment losses (Andreu et al., 1996; Gómez-Rey et al., 2013b; Saá et al., 1994) and to orthophosphate chemisorption on Al, Fe and Mn oxides if the soils are acidic (Certini, 2005), but most probably sediment losses are too low in our experiment to cause a significant P depletion in soils. The concentration of $P_{sediments}$ was almost the same as in ashes and slightly higher than in soils. Compared to our data, in Thomas et al. (1999) soils had similar concentration of P, but the sediments and ashes showed much higher values most probably due to the higher intensity of the fire. Our data on $P_{sediments}$ agrees with the values recorded by Gómez-Rey et al. (2013b), although in the latter study ash levels of P were 6 times higher than those in sediments. Like for N, the application of mulching had no effect on soil and sediment P as also reported by Gómez-Rey et al. (2013b) and Gómez-Rey and González-Prieto (2014).

In general the availability of basic cations and micronutrients increases due to the combustion of soil organic matter and to the accumulation of ashes, but eventually the concentration of these nutrients decreases (Certini, 2005; Khanna et al., 1994). The concentrations of basic cations in sediments were similar to those recorded elsewhere (de Koff et al., 2006; Gómez-Rey et al., 2013b; Robichaud and Brown, 1999; Thomas et al., 1999), although in our case only $Ca_{sediments}$ and $Mg_{sediments}$ decreased with time. While in Gómez-Rey et al. (2013b) ashes were always richer in basic cations than sediments, in the present study ash and sediment levels were within the same range. The addition of mulching does not affect the concentration of basic cations in burnt soils and sediments, although Gómez-Rey et al. (2013a) and Gómez-Rey et al. (2013b) concluded that mulching had little but positive effects on soil K, Mg and Ca mostly by reducing erosion. On the contrary, these authors found that the concentration of basic cations in sediments was not affected by mulching.

In our soils the values for Al, Mn, Mo and Zn were similar to those reported elsewhere (García-Marco and González-Prieto, 2008; Gómez-Rey et al., 2013a; Gómez-Rey and González-Prieto, 2014), whereas Cu was slightly higher compared to these studies and Fe was slightly lower than in Gómez-Rey et al. (2013a) and Gómez-Rey and González-Prieto (2014). For sediments, Mn and Zn were the only trace elements that significantly decreased with time; and when compared to the data from Gómez-Rey et al. (2014), the concentrations in our experiment are similar for Zn, lower for Al, Cu and Fe and higher for Mn. It must be highlighted that, in our case, Mo, Mn and Zn concentrations in sediments exceeded the reference levels for ecosystem protection (CEC, 1986; DEC, 2010; EPA, 2007a, b; Macías Vázquez and Calvo de Anta, 2009), and that might negatively impact the vegetation recolonizing the burnt area and also lead to toxicity risks in the sedimentation area (water and soil) as also suggested Gómez-Rey et al.

(2014). Twelve months after the fire, our sediments had less Al and Fe and more Mn and Zn compared to soils, whereas in Gómez-Rey et al. (2013b) sediments and soil concentrations were similar except for Cu, Mn and Zn, which had higher concentrations in sediments. Levels of trace elements in ashes were in general within the sediment range both in our experiment and in Gómez-Rey et al. (2014), but the absolute concentrations in ashes were 2-6 fold higher in the latter than in present study. The lack of mulching effects on the concentration of micronutrients and trace elements in soils and sediments is in agreement with the data provided by Gómez-Rey et al. (2014).

The PCAs show that both soil and sediment samples change with time according to the measured variables, being the differences among sampling dates more pronounced during the first half of the experiment. Soils sampled 9 and 12 months after the fire cannot be distinguished between them, contrasting with the differences between samples taken 8 and 12 months after the fire in a similar field experiment carried out by Gómez-Rey and González-Prieto (2014). These contrasting results are likely due to differences in site characteristics (soil quality, fire severity, dominance of resprouters or obligate seeders, altitude and orientation of the area), weather conditions (temperature and rain regimes) and relative importance of erosion, as all these factors affect the speed of recovery of the vegetation cover and the characteristics of the soil remaining in situ. Due to a more severe fire and harsher climatic conditions in the field site studied by Gómez-Rey and González-Prieto (2014), burning effects on different soil properties were still noticeable 4 years after the fire (authors unpublished data), while in the present study site values from 2 years after the fire indicate no differences on the measured soil properties compared to t= 12 months (data not shown). The variables most strongly associated with the first two factors are rather similar between the PCA_{soils} and $PCA_{sediments}$ and they are also similar to the PCA loadings in Gómez-Rey and González-Prieto (2014).

The lack of differences among control and mulched plots in the accumulated mass of sediments is most probably due to low erosion rates in our site, where the annual precipitation was 827 mm. These results contrast with those from a similar experiment carried out nearby but under much rainier conditions (3036 mm y^{-1}, Gómez-Rey et al. (2013b)), where the total mass in the accumulated sediments of most of the analysed elements was much higher in their control and seeding plots than: a) in their mulched plots; and b) the amount retrieved in all plots from our experiment (up to 35-fold). Moreover, the mass of nutrients lost by erosion in their mulching plots was similar in magnitude to the losses in all our plots (slightly lower for K, Ca, Mn, Zn, Cu and Mo; similar for total N, NH_4^+, NO_3^- and Na; and slightly higher for Mg, P, Al and Fe). Therefore, it can be concluded that with moderate precipitation rates, erosion of burnt areas is not significantly reduced by mulching addition. This fact should be taken into account when planning where to use this post-fire stabilisation technique, especially considering the costs and difficulties of its application in large or remote burnt areas and also the potential competence with straw use as livestock fodder. Despite the low erosion rates compared to other fires, it should be highlighted again that in the present study burning lead to exceed the reference levels for ecosystem protection of Mo, Mn and Zn in sediments.

The percentage of ash elements lost by erosion could be useful when assessing the potential recovery of vegetation, especially for micronutrients in repeatedly burnt areas where they can become limiting. In our case, $Fe_{sediments}$ and $Zn_{sediments}$ accounted for a high percentage of ash elements lost by erosion. All the studied elements but Mo accounted for a higher percentage of ash elements lost by erosion in our experiment than in the mulching plots from the prescribed fire studied by Gómez-Rey et al. (2013b) and Gómez-Rey and González-Prieto (2014). Despite the much lower erosion rates recorded in our experiment when compared to the prescribed fire, $NO_3^-{}_{sediments}$, $Cu_{sediments}$, $K_{sediments}$ and $Na_{sediments}$ in our plots accounted for an even higher percentage of ash elements than in the control and seeding plots from the prescribed fire. Nonetheless, to compare the two studies in a comprehensive way is rather difficult due to several dissimilarities between both sites: a) slates vs. granitic parent material (i.e. fine textured soil with good aggregation vs. coarse textured soil with weak aggregates, leading to differences in water holding capacity, heat transfer, organic matter stabilisation, etc.); b) S vs. NW orientation, which usually exert a great influence on litter accumulation; c) wildfire vs. prescribed fire with fuel addition; and d) 0.70 kg m^{-2} of ashes collected one month after the fire vs. 1.29 kg m^{-2} of ashes sampled just after the fire. Although precipitation in our study area before ash sampling was low and likely prevented significant losses by lixiviation and runoff, a fraction of ash enriched in some nutrients might have been wind-eroded before ash sampling and treatment application as suggests the rather different ash elemental composition and the proportion ash:sediments for the different elements between the two studies. If this occurred in our experimental site, the percentages of ash elements lost by runoff might be overestimated when compared to other studies without ash losses before sampling.

For most elements, the erosion losses expressed as percentage of nutrient pools in ash+topsoil were within the same range in our study and in the mulched plots of Gómez-Rey et al. (2013b) and Gómez-Rey and González-Prieto (2014), indicating again how low was the erosion rate in the present study.

To sum up, this field experiment after a medium-severity wildfire in a steep area confirms the already suggested hypothesis that mulching has no impact on soil and sediment concentrations of nutrients and trace elements and it does not affect net soil N rates (mineralisation and nitrification). Both soils and sediments change with time in a similar way and it seems that the PCAs including the studied variables can be a useful tool to assess whether burnt soils and the eroded sediments in the area are changing with time and the speed of the change. Despite the low erosion rates due to moderate precipitation, the concentration of Mo, Mn and Zn in sediments is above reference levels for ecosystem protection. However, straw mulching does not have a significant effect in reducing soil erosion and the subsequent loss of nutrients with such low erosion rates; and we found no differences between the plots with straw mulch applied in wide and narrow bands along the contour lines (higher and lower straw dose per plot respectively).

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Section 6

Effects of fire, fire severity and post-fire straw mulching on soil gross N transformation rates

Section 6 is based on the following papers:

Fernández-Fernández, M., Rütting, T., González-Prieto, S. (2016) Effects of a high-severity wildfire and post-fire straw mulching on gross nitrogen dynamics in Mediterranean shrubland soil. *GEODERMA* (Submitted).

Fernández-Fernández, M., Rütting, T., González-Prieto, S. (2017) Fire severity and straw mulching effects on winter and spring soil gross N dynamics in a Mediterranean forest soil. (In preparation).

6.1 Abstract

Little is known about the combined impacts of fire and straw mulching, a widely used post-fire emergency measure, on the soil N cycle. By means of two ^{15}N tracing experiments, gross N transformation rates were quantified with the numerical model *Ntrace* to assess the effects of different burning severities and straw mulching on the N cycle. In the first experiment (Vilameá fire) unburnt (US) and severely-burnt soils without (BS) and with straw mulching (BSM) were preincubated under optimal conditions during 3 and 6 months to accelerate the evolution of the soil-straw mixture. After 3 months of preincubation, gross mineralisation (M_{SON}) and gross NH_4^+ immobilisation (I_{NH4}) in BS more than doubled compared to US and mulching partly mitigated this stimulation in the mineralisation-immobilisation turnover (MIT). After 6 months, MIT differences among treatments disappeared and gross rates approached those in US after 3 months. After three months, autotrophic nitrification (NH_4^+ oxidation) in all treatments was around 10 times lower than MIT, while after 6 months it remained similar in US but increased 8-fold in burnt soils. Heterotrophic nitrification of organic N only occurred in burnt soils, and its importance was similar to autotrophic nitrification after 3 months, but around 4-fold lower after 6 months. Therefore, burning opened up the N cycle and NO_3^- accumulated, increasing the potential for ecosystem N losses; and in the short term, straw mulching slightly mitigated the effects of fire on the N cycle. The second experiment (Palmés fire) included unburnt soil (US) and soils from both medium (BI and BIM) and highly burnt spots (BH and BHM), according to fire severity, which were preincubated for 3 and 6 months with and without straw, but outdoors so weather conditions were as close as possible to those in the field. In US (t=3 months), MIT, heterotrophic nitrification and denitrification were one order of magnitude higher than autotrophic nitrification and DNRA, whereas at t=6 months MIT remained similar, heterotrophic nitrification, DNRA and denitrification increased and autotrophic nitrification slightly decreased. BH and BHM, at t=3 months, presented no heterotrophic nitrification, had a lower MIT than US, autotrophic nitrification was the highest rate and denitrification in BHM was around 2 times higher than in BH; whereas at t=6 months MIT and denitrification increased (highest denitrification rates in the whole experiment), heterotrophic nitrification appeared in BH and autotrophic nitrification slightly decreased. Conversely, at t=3 months BI and BIM had, compared to US, higher MIT and autotrophic nitrification and lower heterotrophic nitrification and denitrification; while at t=6 months BI and BIM presented a new rate (mineralisation of recalcitrant SON) but evolved in different directions. In BI the pattern was similar to BH and BHM, but in BIM the MIT decreased substantially, denitrification was absent, DNRA decreased and heterotrophic nitrification increased. We concluded that fire severity impacts on SOM quantity and quality and on soil microbial communities greatly affected the MIT, and that increased MIT combined with high soil moisture probably limited autotrophic nitrification and promoted DNRA and denitrification through competition for NH_4^+ and O_2 depletion in soil microsites. For the first time, DNRA was reported in burnt soils and it was of similar magnitude to the values reported for the unburnt control. The partitioning of NO_3^- reduction

between DNRA and denitrification in burnt soils might have implications on N retention within the soil system and for greenhouse gas emissions. Straw mulching, by the extra supply of organic matter in the short term and by facilitating plant growth in the longer term, had contrasting consequences (t=3 vs t=6 months) on the N cycle of moderately burnt soils.

6.2 Introduction

Although fire is a natural phenomenon in most terrestrial ecosystems, nowadays most wildfires are caused by humans, either directly through accidents, negligence, arson and side effects of human infrastructures, or indirectly by making ecosystems vulnerable to fire (Bento-Gonçalves et al., 2012; Blaud et al., 2016; Caldararo, 2002; Pausas and Keeley, 2009). Climate change will be one of the most important factors shaping ecosystem functioning in the coming decades (Blaud et al., 2016), and the influence of climate change on the increasing number, extent and severity of wildfires, as well as the feedback mechanisms of fire on climate change, should not be disregarded (Bento-Gonçalves et al., 2012; Birot, 2009; Bowman et al., 2009; Pereira et al., 2011; Robichaud et al., 2010). Many soil properties are affected by fires (Certini, 2005), and burning also influences global C and N cycles due to the release of gases to the atmosphere and to the impacts of fire on the soil system, a key compartment regulating C and N dynamics (Bowman et al., 2009; Wang et al., 2014). Nonetheless, post-fire soil erosion due to the removal of the protective vegetative cover is probably one of the most serious fire outcomes (Blaud et al., 2016; Neary et al., 2008).

Wildfires have a great influence on the soil N cycle because they cause a removal of N from the system through soil organic matter (SOM) combustion, volatilisation of N gases, leaching and erosion. Furthermore, burning modifies the size of N compartments in the soil by converting organic- to inorganic-N, increasing recalcitrant organic N forms and decreasing the most labile ones (Castro et al., 2006). Also, both quantity and specific composition of microbial communities, the main agents of soil N transformations, are affected by fires (Certini, 2005; Fisher and Binkley, 2000; Prieto-Fernández et al., 2004); and altered soil N rates can also promote N losses if denitrification and/or nitrate (NO_3^-) accumulation are favoured (Fierro and Castaldi, 2011; Karhu et al., 2015), with the subsequent on-site fertility problems for plants and increased risk of eutrophication off-site. Despite the large number of factors influencing the response of soil gross N rates to burning (forest type, intensity and frequency of fire, climate, time between fire and sampling, method used to estimate the gross rates, etc.) it seems that in most cases gross mineralisation in burnt soils increases and gross nitrification either decreases or remains similar compared to unburnt controls up to one year after the fire (Gómez-Rey and González-Prieto, 2015; Wang et al., 2014).

One of the emergency stabilization techniques most widely used after wildfires is straw mulching, which has shown an immediate effectiveness in increasing ground cover and thus reducing soil erosion during the first critical months after the fire (Bento-Gonçalves et al., 2012). Both the soil composition and soil processes might be altered by mulching, as it enhances

vegetation recovery (and thus nutrient uptake by plants), modifies the runoff-infiltration ratio, reduces erosion and modifies the topsoil C and N content. In Gómez-Rey et al. (2013a) and Gómez-Rey and González-Prieto (2014) straw application after fire effectively reduced erosion but did not affect the soil nutrient concentrations. Mulching has been shown to affect gross N fluxes in unburnt soils (Cheng et al., 2012b; Huang et al., 2008), but we are aware of only one experiment testing the effect of straw application on gross N rates in burnt soils (Gómez-Rey and González-Prieto, 2015). This study with a soil affected by a moderate to highly severe wildfire showed that mulching resulted in a short-lived stimulation of gross mineralisation and gross immobilisation of NH_4^+.

Soil erosion rates in burnt areas are increased not only due to the destruction of vegetation and the forest floor material, but also because fire often alters water infiltration by enhancing soil water repellency (Doerr et al., 2000; Robichaud et al., 2010). Fire-related sediment yields are usually the highest during the first post-fire year and vary considerably (from 0.1 to 369 Mg ha^{-1} $year^{-1}$) depending on fire severity, climate, vegetation and geomorphic factors (Neary et al. (2008) and references therein). Soil erosion greatly affects soil quality (Gómez-Rey et al., 2013a; Gómez-Rey and González-Prieto, 2014), as well as downslope sedimentation and downstream water quality (Smith et al., 2011); and lately the use of post-fire treatments has increased to mitigate post-fire soil erosion (Robichaud, 2005; Robichaud et al., 2000). However, management operations after fires are not always effective and they might even have a negative effect (Blaud et al., 2016; Neary et al., 2008). Implementation of post-fire stabilization techniques is expensive and labour-intensive, as are the research protocols to assess their efficiency (Robichaud et al., 2010), but there is an urgent need of knowing when, where and how to use these techniques in order to protect burnt soils (Robichaud, 2005). One of the most widely used stabilization techniques is straw mulching, which has shown an immediate effectiveness in increasing ground cover and thus controlling erosion during the first critical months after the fire (Bento-Gonçalves et al., 2012). As any other addition of organic matter to the soil, straw mulching can alter edaphic properties as well as the processes taking place in soils through different mechanisms: modifying the C/N ratio of the SOM, enhancing vegetation recovery and thus nutrient uptake by plants, modifying soil temperature and the runoff-infiltration ratio and preferentially reducing the erosion of some soil fractions (Bautista et al., 2009; Huang et al., 2008). It is already known that post-fire straw addition does not modify nutrient concentrations in soils and sediments (Gómez-Rey et al., 2013a; Gómez-Rey et al., 2013b; Gómez-Rey and González-Prieto, 2014), but information about mulching effects on gross N rates is scarcer and contradictory.

Although field studies on how soil N dynamics are affected by fire and stabilization techniques would be of great value, the patchiness of burnt areas and the difficulties of on-site ^{15}N tracing experiments have usually constrained to laboratory incubations the few research conducted on the topic. The extent of fire impacts on a certain ecological process can be highly variable across the burnt area, and the N cycle comprises several processes mediated by a wide range of microorganisms, which might be affected directly or indirectly by fire in different ways. Therefore, it is pertinent to first develop an experimental design under controlled conditions that

allows to unequivocally assess the effects of fire and straw addition on gross N transformation rates, and afterwards scale up this experimental design to bring together all the other variables that jointly affect the soil N cycle on a field scale. Accordingly, the first aim of this section (Fig. 6.1) was to investigate the effects of high-severity burning and post-fire mulching on soil gross N dynamics from Vilameá fire (high severity fire in summer 2014) by means of a ^{15}N tracer incubation experiment with soils that were kept in the laboratory under optimal conditions of temperature and humidity (24 ℃; 70% WHC) for 3 and 6 months to accelerate the effect of time after the fire. The second aim of this section (Fig. 6.1) was to assess how soil gross N transformation rates are affected by different burning severities and straw addition in weather conditions as close as possible to those in the field and without hampering plant growth and N losses. For that we designed an outdoor experiment in which control unburnt soils and moderately and severely-burnt soils from Palmés fire (summer 2015) were kept for 3 and 6 months in the garden of our institution and then incubated in the laboratory with a ^{15}N tracer to estimate gross N transformation rates.

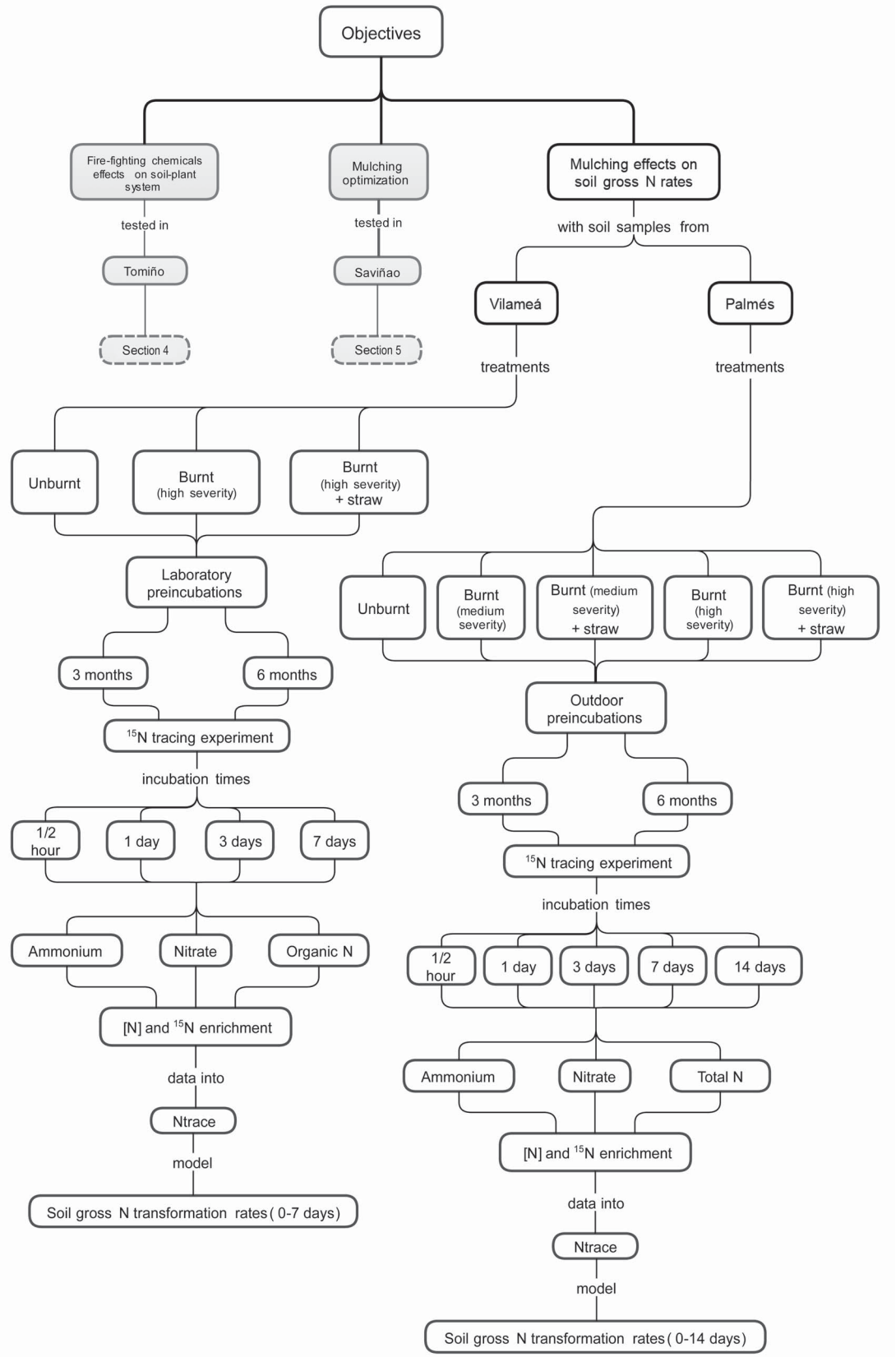

Figure 6.1: Schematic representation of the main objectives of the thesis, highlighting the specific aims, treatments and analyses of the current section.

6.3 Vilameá experiment

6.3.1 Material and methods

6.3.1.1 Site description

Soil samples for the laboratory experiments were collected in the Támega valley at Vilameá (29T $^{06}26$ $^{46}59$, Galicia, NW Spain; Fig. 6.2). The area has a mesic and sub-humid climate with a mean annual temperature of 13-14 ℃ and a mean annual precipitation of 600-800 mm. The area has a bedrock of schist and quartzite and the dominating vegetation is a shrubland of *Ulex europaeus* and *Erica arborea* with scattered *Pinus pinaster* trees. In August 2014 the area was affected by a high severity wildfire that burnt approximately 6 ha of shrubland. Within a distance of 25 m from the burnt place, an unburnt area with the same topography, orientation, vegetation cover and soil type was identified as control for the experiment. Burnt and unburnt soils were characterized as Dystric Leptosol (IUSS Working Group, 2014).

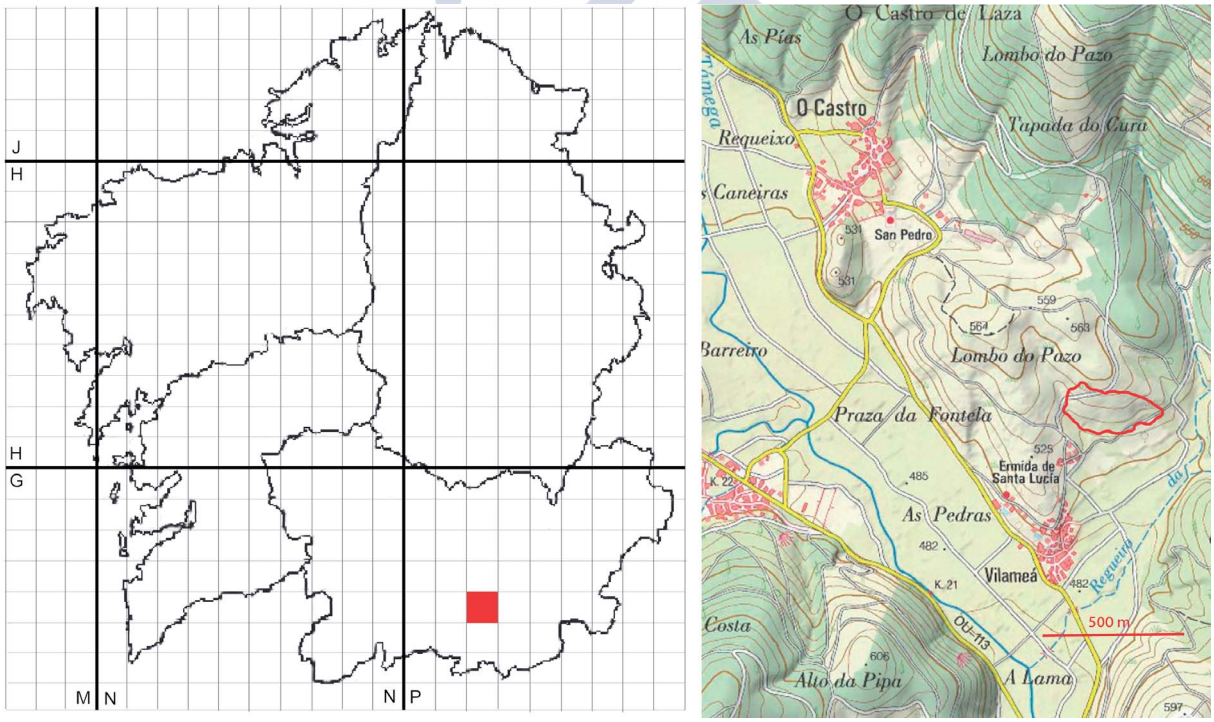

Figure 6.2: Location of the Vilameá experimental field (red square) in the 10x10 km UTM grid map of Galicia (left) and in the topographic map (right).

6.3.1.2 Soil sampling

As the aim was to specifically study the effects of fire and post-fire mulching on the most severely affected area, the day after the fire and with the soil still warm, top soil (0-2 cm depth) was selectively sampled in several spots burnt with high or very high severity (based on Parson et

al. (2010) and Vega et al. (2013a)) considering the following characteristics: a) almost all the pre-fire ground cover and surface organic matter (litter, duff, and fine roots) was consumed; b) the whole burnt surface was covered either with white (or grey) ashes or with bare greyish soil (with reddish spots) exposed; and c) topsoil structure was damaged or destroyed. With this sampling strategy we collected relatively homogeneous sub-samples which were combined into a composite sample, and thus pseudoreplication can restrict the generalisation of our results. For the unburnt control, ten sampling squares (15 x 15 cm) were selected at random and the litter layer (O horizon) and the mineral topsoil (0-2 cm) were separately sampled; soil subsamples were mixed into a composite sample and the same was done with the litter. In the laboratory the soils were sieved (< 2 mm), homogenised and stored at 4 ℃ for soil incubations. For the mulching treatment, wheat straw was harvested in an agricultural field near the burnt shrubland.

6.3.1.3 Soil, litter and straw characterisation

Subsamples of each material were air-dried and finely ground (<100 μm) in a planetary ball mill (Retsch PM100, Retsch GmbH, Haan, Germany, with cups and balls of zirconium oxide). The dry matter content of all samples was assessed by oven-drying sub-samples at 105 ℃ for 5 h and the water holding capacity (WHC) of fresh soils was determined in a Richards' membrane-plate extractor at a pressure of 10 kPa.

Soil pH was measured on air-dried samples with a pH meter (Metröhm, Switzerland) in KCl employing a 1:2.5 soil/solution ratio. Organic N and C of soils, litter and straw were measured on ground samples with an elemental analyser (Carlo Erba CNS 1508). The method for quantifying soil content of NH_4^+-N and NO_3^--N is described in the following section. All analyses were carried out in duplicate (if the coefficient of variation was higher than 5 % the analyses were repeated) and the mean of both analyses for each replicate was used.

Burnt soil has less total C than US (136 vs 146 g kg^{-1} dw; Barreiro et al, 2016), and also a lower WHC (619 ± 7 vs 753 ± 9 g H_2O kg^{-1} dw), but higher values of organic N (9.18 ± 0.12 vs 7.01 ± 0.05 g kg^{-1} dw) and pH_{KCl} (4.10 ± 0.01 vs 3.41 ± 0.01). The initial content of NH_4^+-N was lower in US than in burnt soils (52.9 ± 0.3 and 130.4 ± 0.6 mg kg^{-1} dw, respectively), while the reverse was true for the NO_3^--N (26.0 ± 0.5 and 9.2 ± 2.7 mg kg^{-1} dw, respectively). The C/N ratios of soils and added materials were: unburnt control, 21; burnt soils, 25; litter, 29; and straw, 72.

6.3.1.4 Soil incubation and gross N transformation rates

To assess the effect of burning and straw addition on gross N transformation rates on a temporal basis, an experiment with three treatments (unburnt soil, US; burnt soil, BS; and burnt soil with straw mulching, BSM) and two preincubation times (3 and 6 months) was set up. We did not determine the gross N turnover just after sampling because: a) it would have no sense for one of the three treatments (BSM), because at that moment the straw mulching was still not

applied; and b) all gross N rates in the burnt soil (i.e., two of the three treatments) would likely give nil values, because our research deals with severely burnt (and, thus, sterilized) topsoil sampled immediately after the fire with the soil still hot. After treatment application, soils were preincubated in the laboratory instead of in the field because, as usual, fire severity was extremely heterogeneous throughout the burnt site (in the scale of decimeters) and, consequently, it would be impossible to find the areas burnt with high severity 3-6 months after applying the straw mulching without disturbing the whole burnt area. We are aware of the potential limitations of such an experimental design as it precludes some processes which play an important role in N cycling (physical mixing of soil and straw, plant growth, variable weather conditions). Nonetheless, short- or medium-term incubations are still considered an adequate method to get a picture of the potential capability of the different soils to transform N under optimal conditions (see Abadín et al. (2011) and references therein) and to test the effects of straw on soil N cycling through addition of organic matter via leaching or transfer by fungal hyphae. Before starting the experiment, soils were wetted to slightly below 70% of their WHC with the wetting system described in Gómez-Rey and González-Prieto (2013), which allows easily wetting highly hydrophobic soils. Approximately 2000 g of wet soil per treatment (corresponding to 1600 g of dry soil) were placed in two plastic trays of 20 x 20 x 2 cm (one tray for each preincubation time). For the US and BSM treatments, a piece of nylon mesh (1 mm^2 mesh size) was placed on top of the soil to facilitate the separation of litter and straw from the soil. We added an amount of litter equivalent to 9.59 kg m^{-2} (as in the field) to the US soils, while the BSM received 250 g m^{-2} of straw), a frequently used dose that ensures a soil cover higher than 60% and, thus, effectively reduces erosion. The trays were covered (but not sealed) with filter paper and aluminium foil to regulate water evaporation and incubated in a chamber in darkness at 25 ℃. Throughout the preincubation the humidity of the soils was adjusted to the initial value two times a week by adding around 20 ml water as simulated rain, i.e. allowing lixiviation through the litter layer (US) and the straw mulch (BSM).

After each preincubation period, soils were thoroughly homogenised and a paired ^{15}N labelling experiment, with $^{15}NH_4NO_3$ and $NH_4{}^{15}NO_3$ as tracers and four incubation times (0.5 h, 1, 3 and 7 days), was conducted. Aliquots equivalent to 30 g of dry soil were placed in a total of 144 centrifuge bottles (250 ml): three treatments, two preincubation times, two ^{15}N-tracers, four incubation times and three replicates. The bottles were filled with 4 successive layers of soil, each of which received 1 ml of ^{15}N-tracer solution added uniformly over the soil surface with an automatic pipette (i.e. 4 ml per bottle), equivalent to an N addition of 1 mg kg^{-1} dry soil with a ^{15}N excess fraction of 49 %. After labelling, soils were incubated at 25 ℃ in darkness. Once incubated, soils were extracted with 150 ml KCl 2M (1:5 soil:solution ratio) shaken for 1 h and passed through glass microfibre filters (Whatman GF/A, 125 mm diameter). For NH_4^+-N and NO_3^--N quantification, an extraction-diffusion method described in Fernández-Fernández et al. (2015) was used. After the two titrations (for NH_4^+ and NO_3^-), the resulting $(NH_4)_2SO_4$ solutions were evaporated to dryness at 60 ℃ in a vacuum oven (Memmert VO400, PM400) for obtaining $(NH_4)_2SO_4$ crystals. To accelerate the drying process, the oven was alternatively

under vacuum (15 kPa) and atmospheric pressure. In order to trap possible traces of atmospheric NH_3, the incoming air was passed through a column of activated charcoal. The $(NH_4)_2SO_4$ crystals were finally packed into tin capsules and analysed for ^{15}N. The soil remaining in the flasks and the filters during the extraction procedure was washed with deionized water until no chlorides were detected (silver nitrate test), oven-dried at 105 ℃, finely ground (<100 μm) and packed into tin capsules for organic N analyses. The ^{15}N enrichment of NH_4^+-N and NO_3^--N, as well as the organic N content and its ^{15}N enrichment were measured with an elemental analyser (Carlo Erba CNS 1508) coupled on-line with an isotopic ratio mass spectrometer (Finnigan Mat, delta C, Bremen, Germany). An elemental reference material (Soil 3 from Eurovector, Milano, Italy) and an isotopic standard (IAEA-N1, IAEA-N2, IAEA 305-A, IAEA 305-B and IAEA 311, alternately, from the International Atomic Energy Agency, Vienna, Austria) were included in each set of 10 samples to check the accuracy of the results; if necessary, drift correction was made against internal standards during the run.

6.3.1.5 ^{15}N-tracing model

Gross N transformation rates have been calculated with either analytical or numerical methods by adding ^{15}N-tracers to the soil and then measuring the N pool sizes and their ^{15}N enrichment over a certain incubation period (Murphy et al., 2003). With numerical solutions more N transformations can be estimated simultaneously, different process kinetics can be considered and there is no amplification of errors. However, most of the studies on gross N rates in burnt soils have used analytical methods instead of numerical models (Gómez-Rey and González-Prieto, 2013). The ^{15}N tracing model *Ntrace* (Müller et al., 2007; Rütting and Müller, 2007) used in this experiment is one of the latest developments and allows a more complex description of the soil N processes as a large number of parameters can simultaneously be estimated (Rütting and Müller, 2007). It basically consists on a set of differential equations solved by numerical methods and non-linear fitting routines which search for rate parameters that minimize the misfit between modelled data and a set of observed data and avoid trapping in local minima (Rütting and Müller, 2007). The main differences between the gross rates we present here and those reported in other studies on burnt soils are: 1) we estimated gross autotrophic and heterotrophic nitrification separately, the latter referring to NO_3^- production from SON without mixing into the free soil NH_4^+ pool (Fig. 6.3); 2) we quantified gross NH_4^+ immobilisation and immobilisation of NO_3^- to SON separately; and 3) rates are estimated for the whole incubation period instead of sequentially.

To quantify gross N transformation rates for each of the treatments and preincubation times, a *Ntrace* compartment model with different N pools and possible N transformations was suggested as a start point. To identify the best option describing the measured data, the model was run several times changing the number of considered processes and the Akaike information criterion was used to choose the final model (Staelens et al., 2012). The parameters of the selected transformation rates were estimated using a Markov chain Monte Carlo (MCMC) method by

fitting the model values to the measured contents and ^{15}N enrichments of NH_4^+ and NO_3^- (Müller et al., 2007). The optimisation procedure results in probability density functions (PDFs) from which parameter averages and standard deviations were calculated (Müller et al., 2007). For transformations following first order kinetics, average rates were calculated by integrating gross N rates over the experimental period divided by the total time (Rütting and Müller, 2007). Standard errors of means were calculated based on autocorrelation as described in Harmon and Challenor (1997). Statistical significance in differences between treatments was tested by an overlap of the 85% confidence intervals (CI) (Payton et al., 2000; Rütting et al., 2010).

The final model considered three N pools in all treatments: SON, NH_4^+ and NO_3^- (Fig. 6.3). Unburnt controls (US) retained four transformation rates: mineralisation of SON to NH_4^+ (M_{SON}; zero order kinetics), immobilisation of NH_4^+ to SON (I_{NH4}; first order kinetics), immobilisation of NO_3^- to SON (I_{NO3}; first order kinetics) and oxidation of NH_4^+ to NO_3^- (autotrophic nitrification, O_{NH4}; first order kinetics), whereas burnt soils (BS and BSM treatments) also presented oxidation of SON to NO_3^- (heterotrophic nitrification, O_{SON}; zero order kinetics).

The ^{15}N tracing model is set up in Simulink (The Math Works Inc.) and it is summoned by the MCMC optimisation routine programmed in MatLab (The Math Works Inc.). Initial NH_4^+ and NO_3^- pool sizes and ^{15}N enrichments were estimated by back-extrapolation of the measured values from the first two time-points (0.5 hours and 1 day) (Müller et al., 2004).

6.3.2 Results

6.3.2.1 Inorganic N content

During the preincubation, the content of inorganic N (NH_4^+-N plus NO_3^--N) increased in all soils. At t=3 months burnt soils had 1.2 times more inorganic N than the unburnt control, but 3 months later the opposite pattern was recorded. The content of NH_4^+-N in US increased with preincubation time (Fig. 6.3). Both BS and BSM showed similar contents of NH_4^+-N, which were 2-fold (t=3 months) and 1.3-fold (t=6 months) higher than at t=0 months (130.4 ± 0.6 mg kg^{-1}). Compared to initial values (26.0 ± 0.5 mg kg^{-1}), the unburnt soil had 3.7 and 5.2 times more NO_3^--N after 3 and 6 months, respectively (Fig. 6.3), while BS and BSM had approximately 1.4 times more NO_3^--N at t=3 months compared to initial values (9.2 ± 2.7 mg kg^{-1}), but up to 14 times more NO_3^--N after 6 months of preincubation (Fig. 6.3). Therefore, for US the contribution of NH_4^+-N to the inorganic N pool increased with preincubation time from 59% (t=3 months) to 65% (t=6 months), whereas for BS and BSM treatments NH_4^+-N accounted for most of the total inorganic N at t=3 months (95%) but much less after 6 months of preincubation (57%).

6.3.2.2 Gross N transformation rates

In general, there was a good fit between the output of the ^{15}N tracing model and the measured data (Figs. 6.4, 6.5, 6.6, 6.7, 6.8 and 6.9). All gross N rates are expressed on a soil dry weight (dw) basis. For each N transformation rate, the percentage of difference between treatments and preincubation times is calculated considering as reference value the following: a) t=3 months when comparing the rate of each treatment between both preincubation times; b) US when assessing the effect of fire; and c) BS when assessing the effect of mulching. For each gross N rate, all differences tested (by an overlap of the 85% CI) were significant both between treatments (same preincubation time) and between preincubation times (same treatment).

The mineralisation rate of SON to NH_4^+ (M_{SON}) at the 3 months preincubation in the unburnt control was 4.82 ± 0.08 mg N kg^{-1} dw day^{-1}, and burning had a positive effect on the rate, which was 133% higher in BS than US (Fig. 6.3). Mulching decreased M_{SON} by 37% (BSM compared to BS). At t=6 months, M_{SON} was reduced in the three treatments compared to t=3 months, but to a different extent: 16% in US, 70% in BS and 42% in BSM. As a result, the differences between treatments in M_{SON} after 6 months of preincubation were always below 20% (Fig. 6.3).

Gross immobilisation of NH_4^+ to SON (I_{NH4}) followed a similar pattern as M_{SON} (Fig. 6.3). At t=3 months BS had 216% higher I_{NH4} than US (3.01 ± 0.12 mg N kg^{-1} dw day^{-1}) and in BSM it was 128% higher than in US, but 28% lower than in BS. Three months later, I_{NH4} in BS and BSM was around 60% lower while in US it remained similar. Therefore, by the end of the experiment there were relatively small differences (<11%) in I_{NH4} among treatments.

As all plausible N rates, oxidation of SON to NO_3^- (heterotrophic nitrification) was considered during the modelling of all treatments. In US, O_{SON} was discarded after several runs of the model because the values yielded by the model (usually 10000-50000 iterations) were close to 0 and did not follow a normal distribution; moreover, the misfit function was 11% higher when O_{SON} was included in the model. However, in BS and BSM, O_{SON} estimates were above zero and normally distributed; and the inclusion of this rate increased the global performance of the model (higher percentage of parameter sets accepted, around 15% reduction of the misfit function and better fit of the modelled and experimental data). At t=3 months O_{SON} was 0.55 ± 0.06 mg N kg^{-1} dw day^{-1} for BS and 0.41 ± 0.08 mg N kg^{-1} dw day^{-1} for BSM, whereas three months later it was 95% (BS) to 167% (BSM) higher (Fig. 6.3).

The differences between treatments in the oxidation rate of NH_4^+ to NO_3^- (autotrophic nitrification) were small at t=3 months and became larger in burnt soils after 6 months of preincubation (Fig. 6.3). Autotrophic nitrification at t=3 months was the same for US and BS (0.53 ± 0.02 mg N kg^{-1} dw day^{-1}), whereas in BSM it was 20% lower. At t=6 months US showed a slightly lower autotrophic nitrification, but both BS and BSM showed higher rates (6- and 8-fold respectively) compared with the previous preincubation time. As a result, at t=6 months burnt soils had on average 7-fold higher nitrification rates than US and mulching had no effect on this rate. In BS and BSM, the O_{NH4}/O_{SON} ratio increased from 1 at t=3 months to 3.4 after 6 months of preincubation.

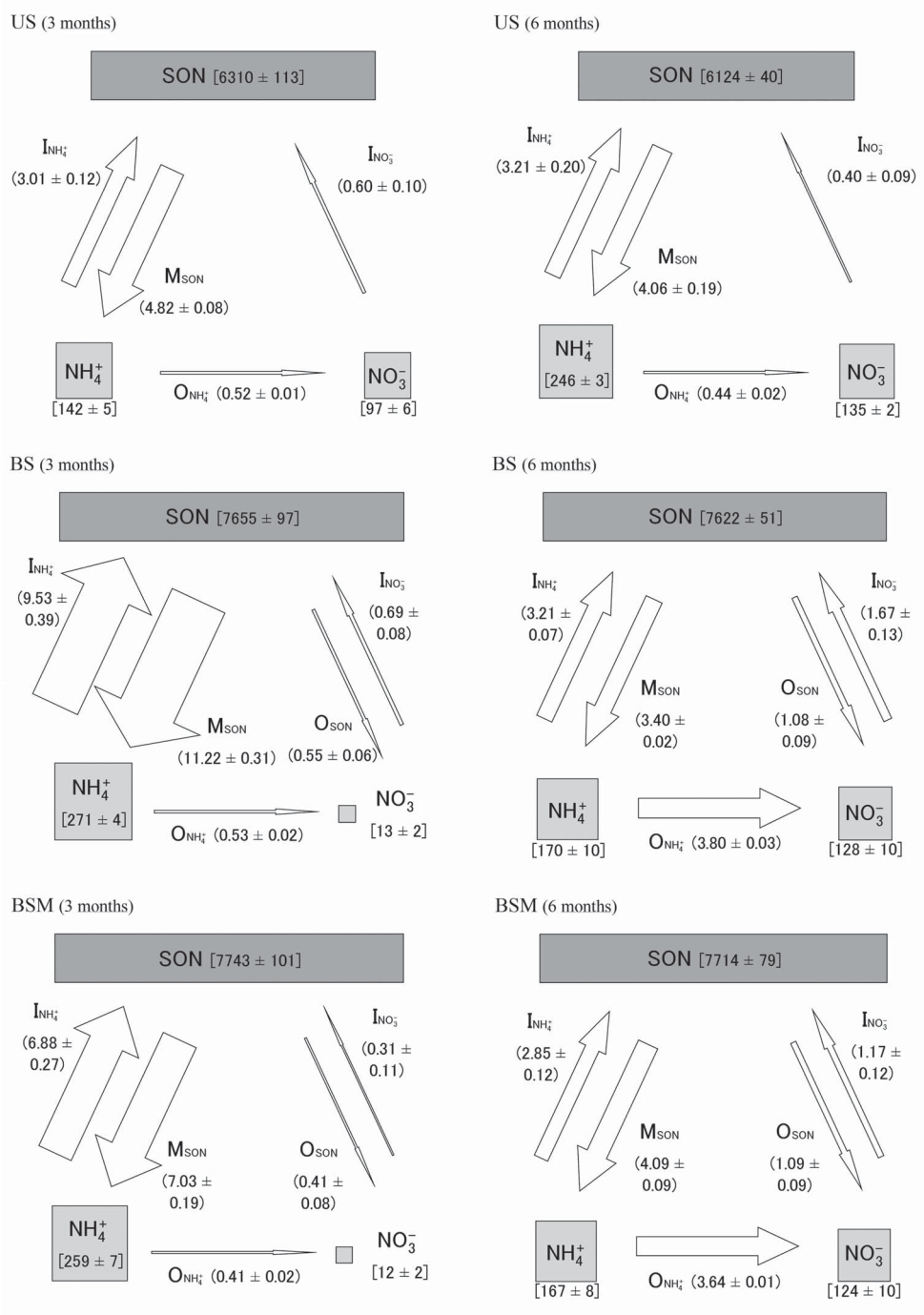

Figure 6.3: Gross N transformation rates (mg N kg^{-1} dw day^{-1}; mean ± S.D.) and size of N pools (mg N kg^{-1} dw; mean ± S.D.) for US, BS and BSM after 3 and 6 months of preincubation. Box size is proportional to the N pool size (1:1) except for SON (1:10). The width of the arrows is proportional (1:1) to the estimated gross N transformation rates. Key: US, unburnt soil; BS, burnt soil; BSM, burnt soil with mulching; SON, soil organic N; M_{SON}, mineralisation of SON to NH_4^+; I_{NH4}, immobilisation of NH_4^+ to SON; I_{NO3}, immobilisation of NO_3^- to SON; O_{NH4}, autotrophic nitrification or oxidation of NH_4^+ to NO_3^-; O_{SON}, heterotrophic nitrification or oxidation of SON to NO_3^-.

Compared to I_{NH4}, I_{NO3} behaved in a quite different way (Fig. 6.3). In the t=3 months experiment I_{NO3} in US was 0.60 ± 0.10 mg N kg^{-1} dw day^{-1}, whereas in BS it was 15% higher. Straw mulching decreased I_{NO3} by 55% when compared to BS and by 48% when compared to US. At t=6 months I_{NO3} was 34% lower than at t=3 months in US, but 142-274% higher in BS and BSM, leading to larger differences in this rate between treatments at t=6 months (+321% for BS vs. US; +194% for BSM vs. US; and -30% for BSM vs. BS).

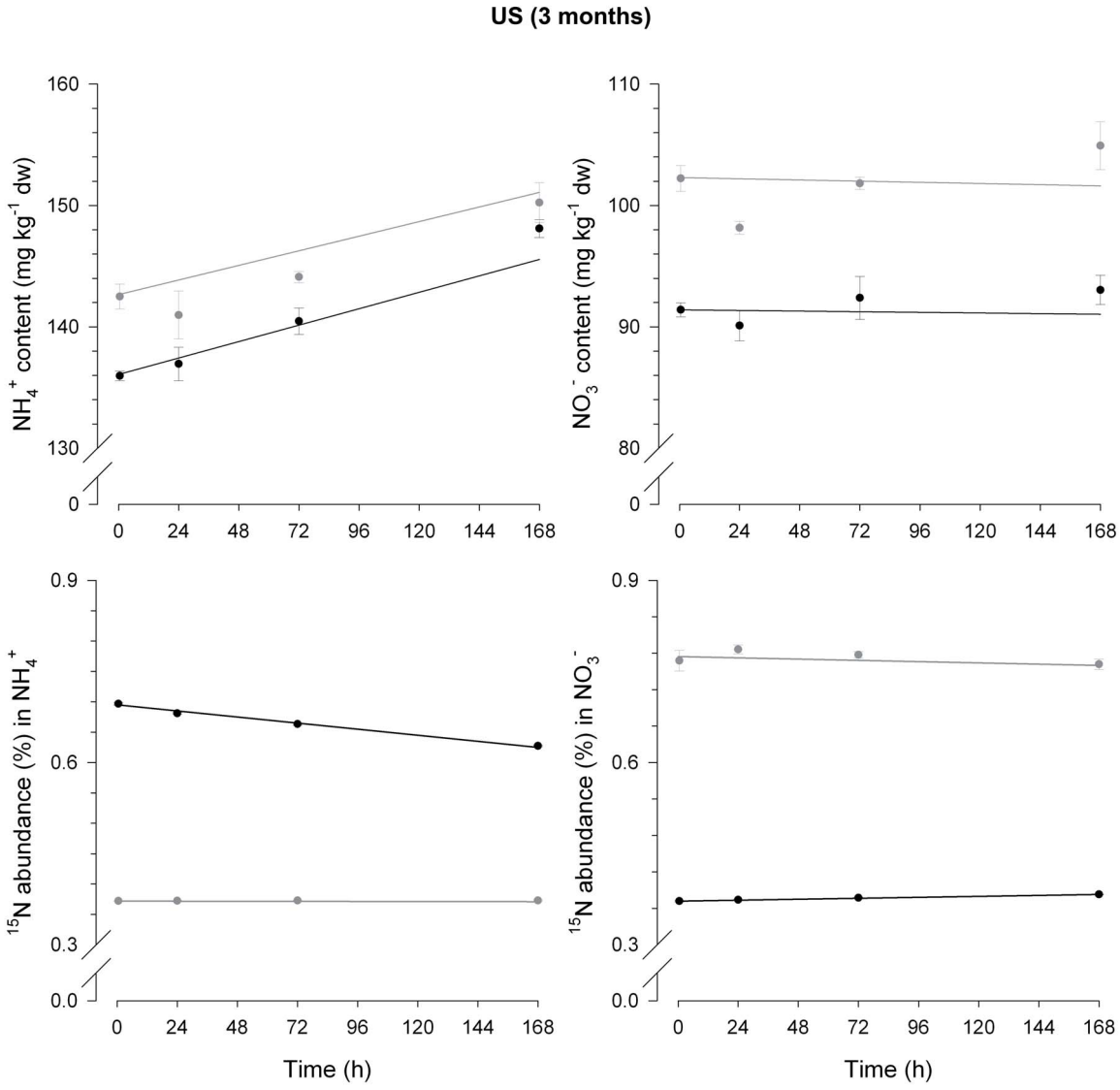

Figure 6.4: Model fit for the unburnt soil (US) at t=3 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N and the ^{15}N abundance in NH_4^+ and NO_3^- pools (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

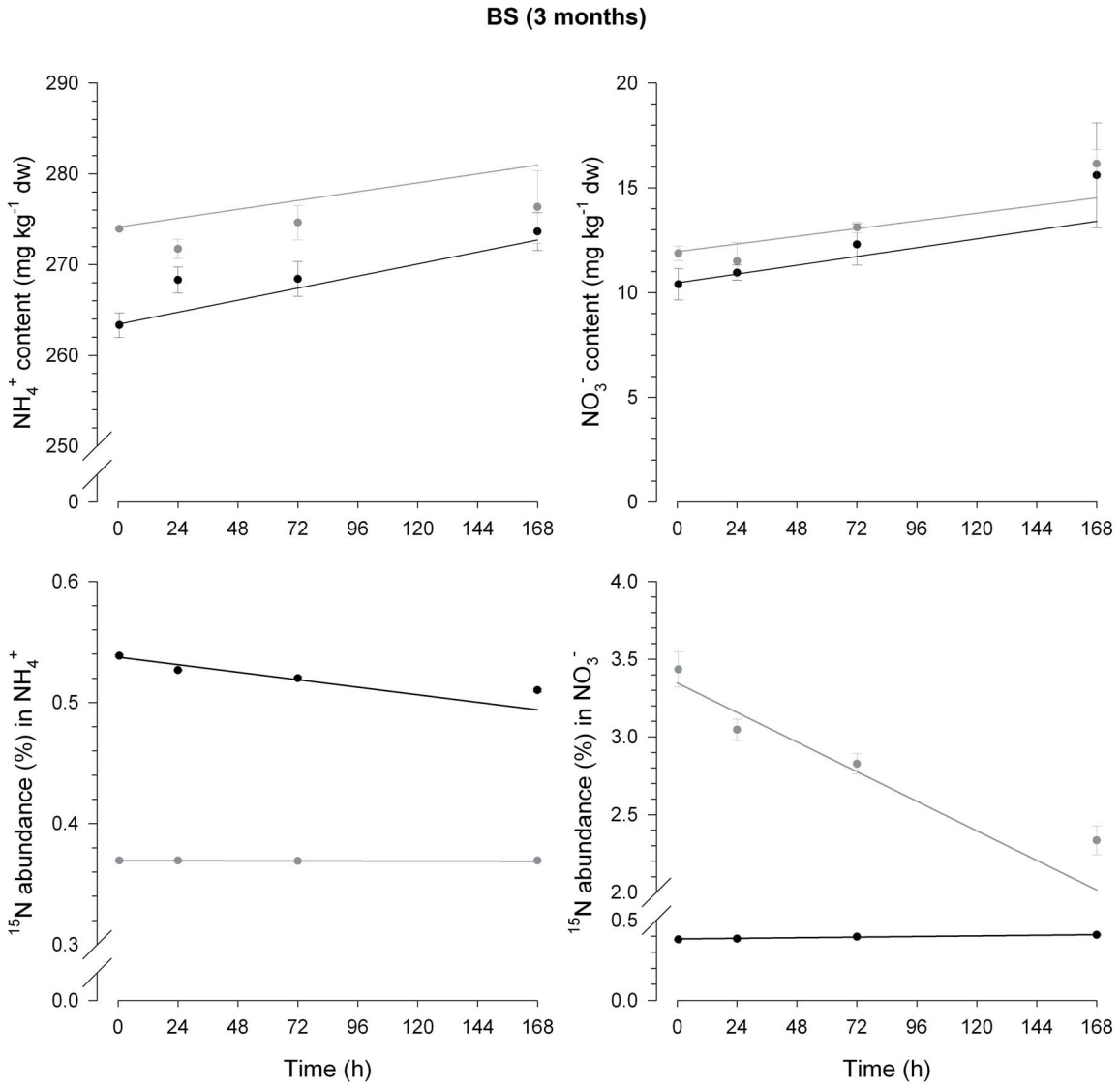

Figure 6.5: Model fit for the burnt soil without mulching (BS) at t=3 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N and the ^{15}N abundance in NH_4^+ and NO_3^- pools (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

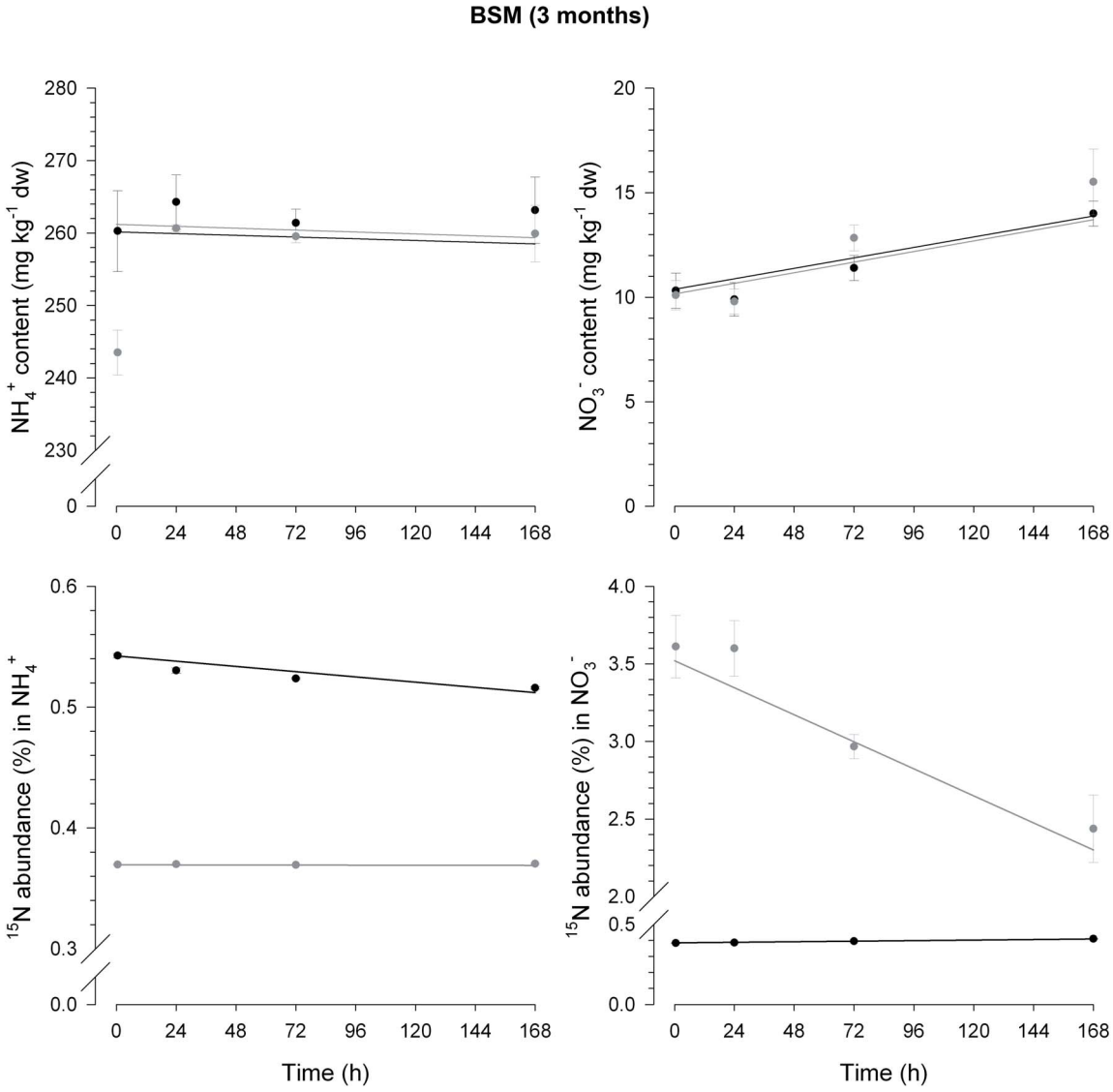

Figure 6.6: Model fit for the burnt soil with mulching (BSM) at t=3 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N and the ^{15}N abundance in NH_4^+ and NO_3^- pools (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

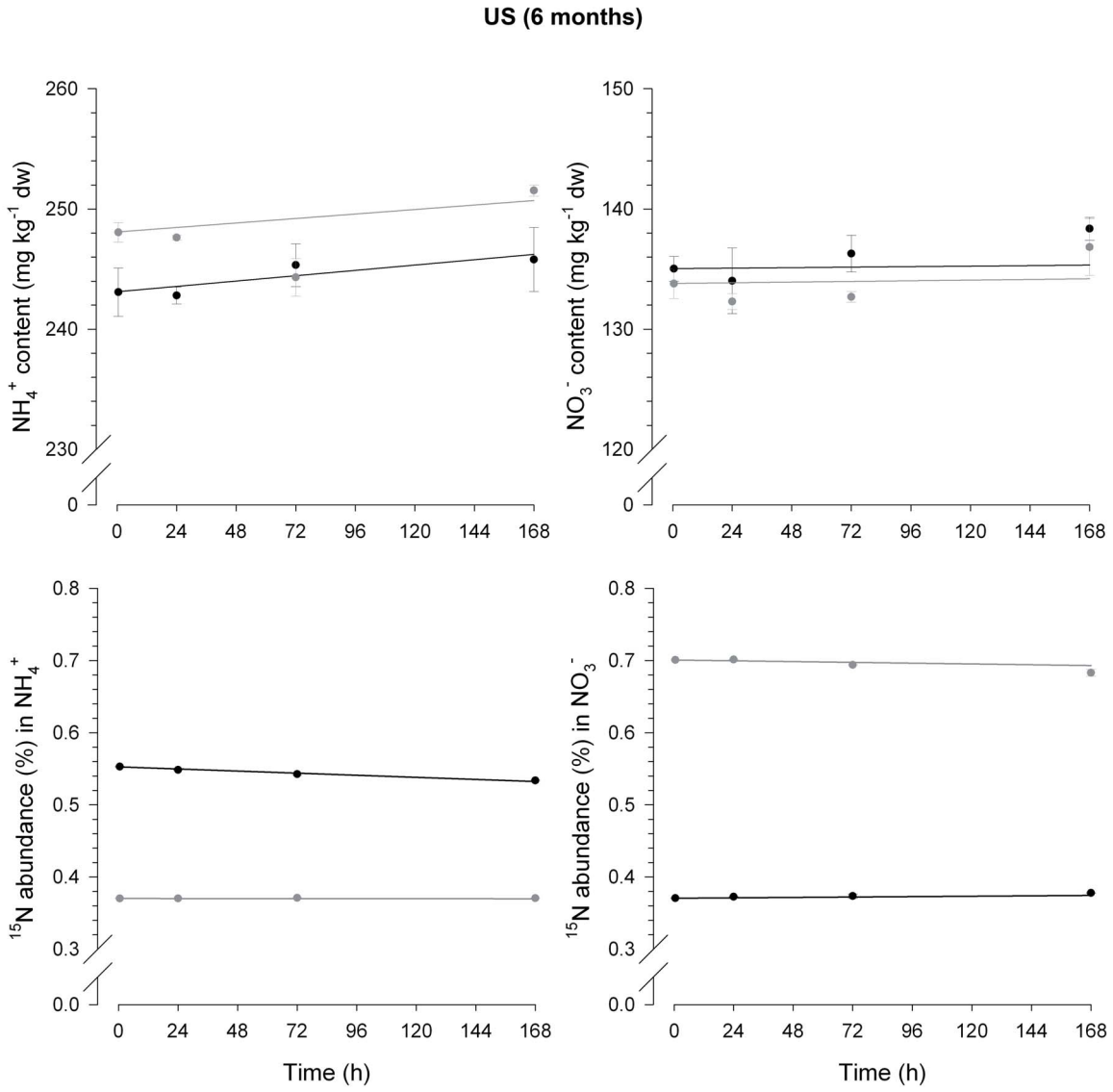

Figure 6.7: Model fit for the unburnt soil (US) at t=6 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N and the ^{15}N abundance in NH_4^+ and NO_3^- pools (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

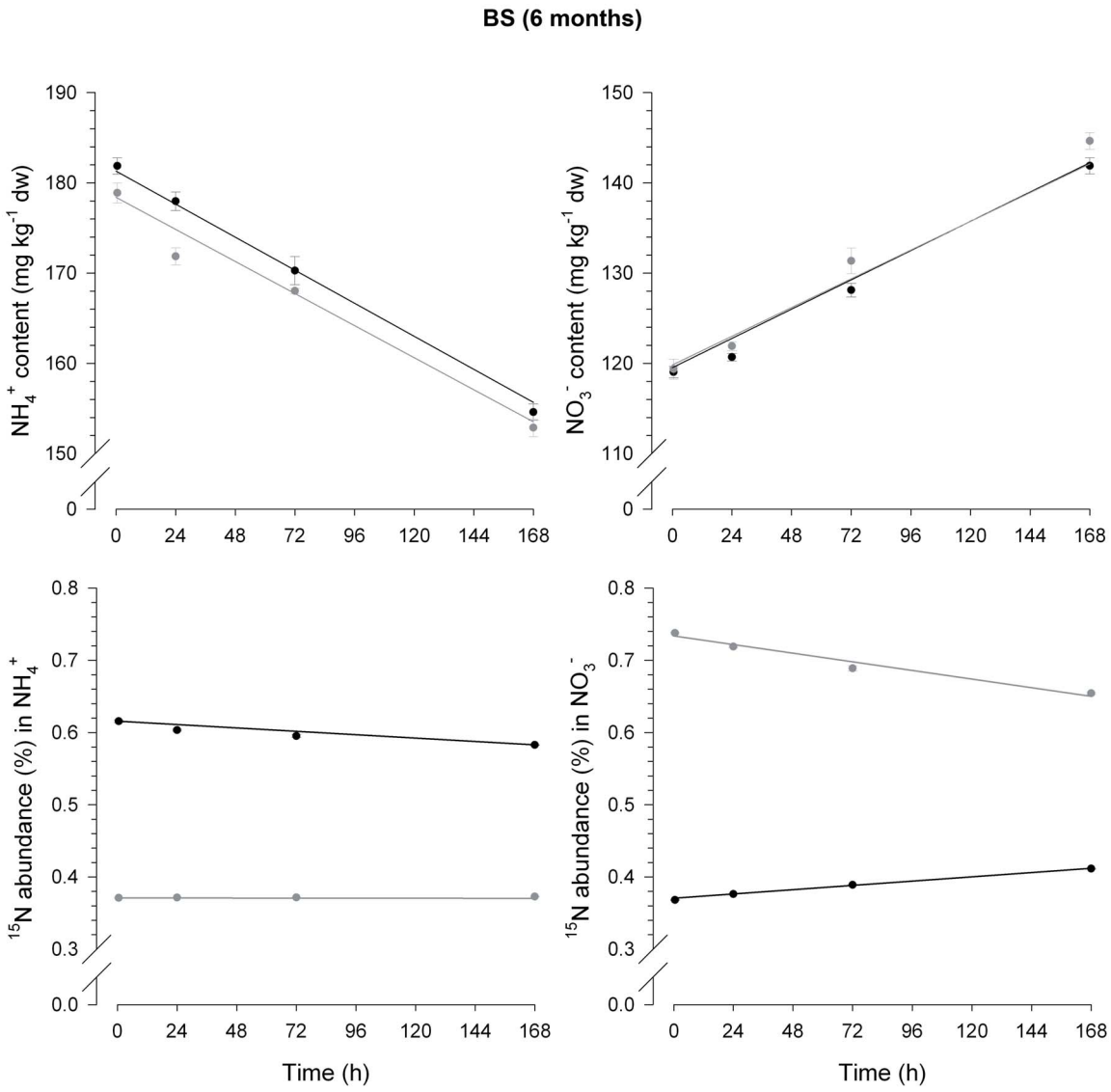

Figure 6.8: Model fit for the burnt soil without mulching (BS) at t=6 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N and the ^{15}N abundance in NH_4^+ and NO_3^- pools (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

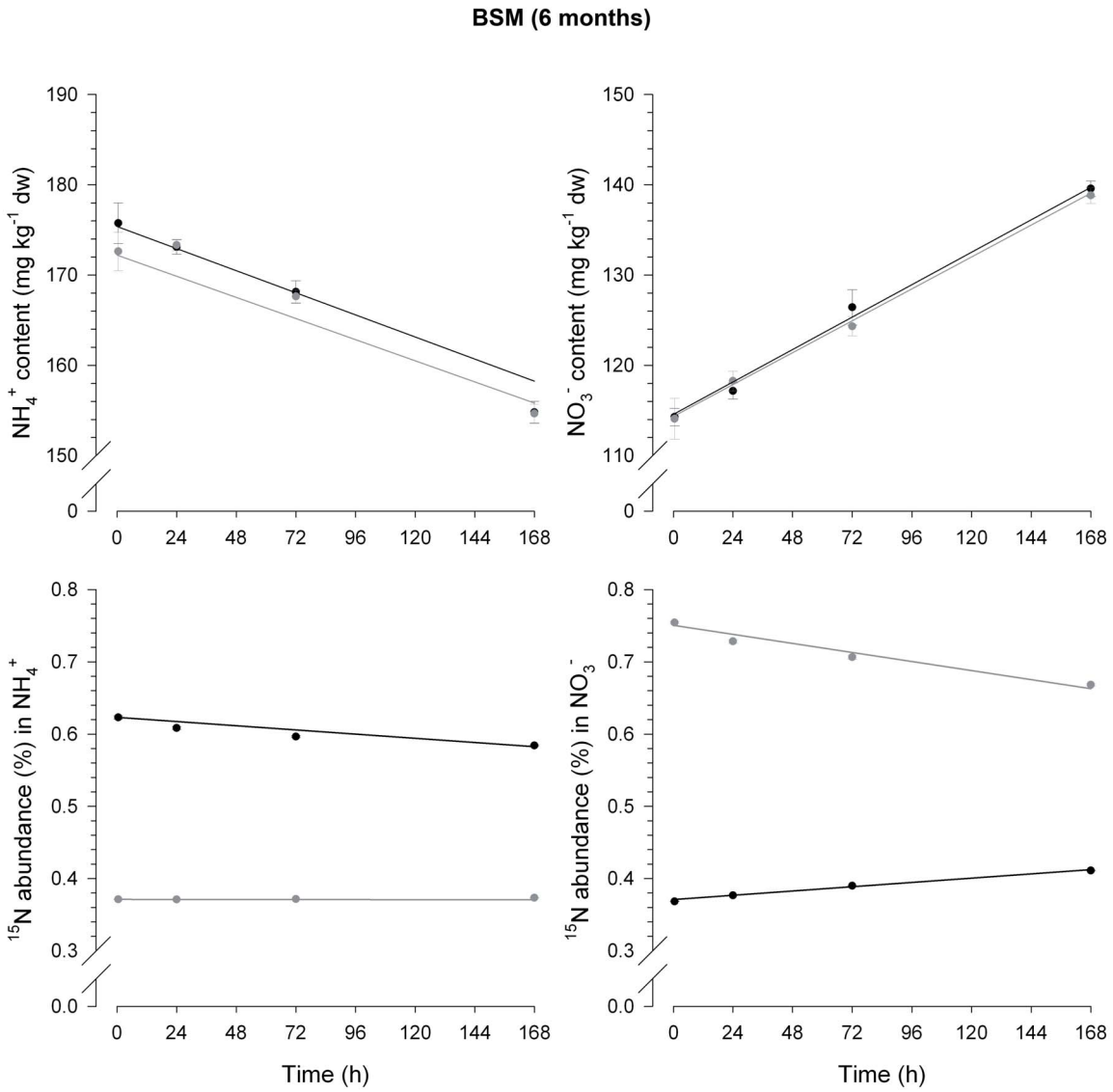

Figure 6.9: Model fit for the burnt soil with mulching (BSM) at t=6 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N and the ^{15}N abundance in NH_4^+ and NO_3^- pools (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

6.3.3 Discussion

Both high-severity fire and preincubation length affected the total inorganic N, NH_4^+-N and NO_3^--N content in soil. The higher inorganic N content and higher NH_4^+/NO_3^- ratio (BS 13:1; US 2:1) in the burnt soil right after the fire is in agreement with the widely reported increased soil inorganic N concentrations after fire (see Wang et al. (2014) and references therein), especially that of NH_4^+, a direct product of combustion, whereas NO_3^- requires nitrification to be formed (Karhu et al., 2015). In incubation experiments without plants and under optimal conditions for N mineralisation, in which N losses are largely reduced, an increase in inorganic N concentration

is usually reported (Abadín et al., 2011). In US, a sustained parallel increase in both NH_4^+ and NO_3^- and a rather stable NH_4^+/NO_3^- ratio during the whole experiment was observed, suggesting that both net mineralisation and net nitrification were fairly constant. On the contrary, in burnt soils the total amount of inorganic N increased up to 3 months and then remained stable, and the evolution of NH_4^+ (rapid increase followed by rapid decrease) and NO_3^- (initially stable and then fast increase) diverged during the whole preincubation. Both the reduction of the NH_4^+ pool and the larger NO_3^- pool in burnt soils might indicate that the source of labile organic matter is being depleted, slowing down heterotrophic mineralisation and/or benefiting autotrophic nitrification which do not depend on organic C (see González-Prieto et al. (1991) and Verhagen et al. (1995)).

These changes in inorganic N content in soils after fires are due to alterations (quantitative and qualitative) in gross N fluxes, most probably related to a changed microbial community and activity, as reported for the same soils by Barreiro et al. (2016). These authors found that burning had a large impact on the microbial community structure and negatively affected total microbial biomass, but increased soil respiration, as well as bacterial and fungal growth. Likewise, Goberna et al. (2012) recently demonstrated that archaea, bacteria and fungi respond differently to fire and that alterations in the microbial community structure are the main driver of post-fire changes in microbial biomass and total activity, determining the alteration of soil biogeochemical processes. Both positive and negative effects of fire on soil microbial biomass and activity have been reported (Acea and Carballas, 1996; Díaz-Raviña et al., 2012; Goberna et al., 2012; Vázquez et al., 1993; Yeager et al., 2005), likely due to site-specific characteristics (fire severity, soil moisture, pH...). The positive effect of fire on the MIT (M_{SON} and I_{NH4}) after 3 months of preincubation agreed with most studies dealing with short-term fire impacts on gross N rates (Anderson and Poth, 1998; Neill et al., 1999). However, we observed that enhanced MIT after fire was short-lived, as after 6 months of preincubation no difference between treatments was observed (Fig. 6.3). Indeed, a study in a Mediterranean ecosystem also showed a transient short-term increase of gross N mineralisation, which was no longer noticeable 6 months after burning (Karhu et al., 2015). In the study by Bastias et al. (2006) in Australian forest soils, 3 months after fire gross N mineralisation was lower in burnt soils compared to the unburnt control, but 2 years later the difference was no longer significant. In a study conducted close to our sampling site (Gómez-Rey and González-Prieto, 2013; Gómez-Rey and González-Prieto, 2015), MIT was higher in burnt plots from the first week up to a year after the fire, and differences decreased with time as in our study. Similarly, in several experiments spanning from 6 to 12 months after burning gross N mineralisation was higher in burnt soils (Aranibar et al., 2003; Dannenmann et al., 2011; Kaye and Hart, 1998), although higher gross NH_4^+ immobilisation was only found in Dannenmann et al. (2011). However, all these studies calculated NH_4^+ immobilisation as NH_4^+ consumption minus nitrification and thus NH_4^+ immobilisation might be underestimated if heterotrophic nitrification of organic N was taking place (Dannenmann et al., 2011).

Enhanced MIT is usually explained by higher post-fire availability of organic matter and inorganic N, lower plant competition and absence of plant allelopathic compounds inhibiting microbial activity (Dannenmann et al., 2011) or by the higher activity of the soil microorganisms that survived the fire (Díaz-Raviña et al., 2012). Other studies assessing the short-term effects of burning on soil microbial communities show greatly increased microbial densities compared to the unburnt control, particularly of ammonifying (or N mineralizing) microorganisms (Acea and Carballas, 1996; Goberna et al., 2012; Vázquez et al., 1993). However, the positive effect on ammonifiers almost disappeared 1 year after the fire (Acea and Carballas, 1996), most probably due to the reduction of labile SON in burnt soils (Prieto-Fernández et al., 2004), which agrees with our observation of no stimulation of M_{SON} and I_{NH4} after 6 months of preincubation.

Post fire mulching led to a decreased MIT compared to non-mulched burnt soils in the 3 months preincubation, but these differences disappeared three months later. Contrastingly, in Gómez-Rey and González-Prieto (2015) the MIT was higher in mulched plots compared to the controls (unburnt and burnt without mulching) 4 months after the fire, although there were no mulching effects on soil microbial biomass and activity (Díaz-Raviña et al., 2012). Although in both studies ^{15}N incubations were in the laboratory, it should be pointed out that Gómez-Rey and González-Prieto (2015) sampled soils from the field site 4, 8 and 12 months after fire and mulching, whereas we preincubated in the laboratory for 3 and 6 months soils sampled just after the fire. Other studies testing the effect of mulching in unburnt soils (Huang et al., 2008; Shindo and Nishio, 2005; Watkins and Barraclough, 1996) also report higher gross mineralisation, gross N immobilisation and increased microbial functional diversity in mulched soils due to the extra supply of organic C and N from straw.

Gross oxidation of NH_4^+ to NO_3^- (O_{NH4}; autotrophic nitrification) was not affected by fire after short-term preincubation, whereas after long-term preincubation burnt treatments showed a much higher O_{NH4} than US. Accordingly, Acea and Carballas (1996) found that the nitrifiers density in a forest soil one month after fire did not differ from the unburnt controls, but one year later ammonium oxidizers were positively affected. In another study on forest soils, ammonium-oxidizing bacteria were more abundant in burnt soils even 12 years after fire (Ball et al., 2010). While Goberna et al. (2012) found a short-term increase of the nitrifying population, Yeager et al. (2005) have reported a decrease of soil biomass in general and of ammonia-oxidizers in particular in an experiment spanning from 1 to 14 months after the fire, especially in severely-burnt soils. The second nitrification pathway quantified in our experiment, oxidation of SON to NO_3^- (O_{SON}) (see Barraclough and Puri (1995) for assumptions and possible limitations), only took place in burnt soils. A possible explanation for this finding could be that burning favoured the community of heterotrophic nitrifiers due to the increased pH, increased nutrient availability, changes in quality/quantity of SON or changes in the soil microbial community (no/less competitors in burnt soils). While at t=3 months O_{SON} was slightly lower in BSM than BS, three months later no differences between the two burnt soils were observed. Although O_{SON} doubled from 3 to 6 months, its contribution to NO_3^- production was similar to autotrophic nitrification at t=3 months, but around 4-fold lower at t=6 months,

indicating an increased relative importance with time of autotrophic nitrification as source of NO_3^-.

As most studies quantify gross nitrification by the ^{15}N pool dilution technique, which cannot distinguish between autotrophic and heterotrophic nitrification (Barraclough and Puri, 1995), there is no available data with which to compare our results. Therefore, we calculated gross total nitrification (O_{NH4} + O_{SON}), which was 2-fold (t=3 months) and 11-fold (t=6 months) higher in burnt soils compared to US. These results contrast with those from another experiment in Galicia, in which gross nitrification rates were very low in the unburnt control and not detectable in burnt plots (Gómez-Rey and González-Prieto, 2013; Gómez-Rey and González-Prieto, 2015). In Brazilian soils burning also reduced gross nitrification, although a fast recovery was observed after 45 days (Anderson and Poth, 1998). Other studies report no significant differences in gross nitrification between burnt and unburnt soils (Aranibar et al., 2003; Kaye and Hart, 1998; Neill et al., 1999). However, our results agree with the higher gross nitrification rates reported 6 months after a fire in an Italian shrubland (Dannenmann et al., 2011). Neither gross autotrophic nitrification nor gross total nitrification was affected by mulching in our study. This finding is consistent with the results of a similar experiment by Gómez-Rey and González-Prieto (2015), and those of Huang et al. (2008) and Shindo and Nishio (2005) in unburnt soils. However, Cheng et al. (2012b) found a suppression of gross nitrification by mulching in unburnt soils.

In unburnt soils, I_{NO3} was nearly equal to total gross nitrification, while nitrification exceeded I_{NO3} in burnt soils, even though I_{NO3} after 6 months of preincubation was higher in burnt soils than US. Although our soils have been preincubated under optimal conditions in a closed system (i.e. without N leaching and plant uptake), the fast build-up of the NO_3^- pool in burnt soils between 3 and 6 months supports the evidence of long-term NO_3^- accumulation in burnt soils (Koyama et al., 2012), which exacerbates the risk of ecosystem N losses via NO_3^- leaching (Bladon et al., 2008; Stephan et al., 2012) or denitrification (Karhu et al., 2015). Contrastingly Gómez-Rey and González-Prieto (2013) and Gómez-Rey and González-Prieto (2015) observed a sharp decrease in NO_3^- immobilisation immediately after the fire that persisted at least for a year. Despite the wide differences in the experimental design and the model used, mulching decreased I_{NO3} both in our study and in the one by Gómez-Rey and González-Prieto (2015), although in the latter experiment Díaz-Raviña et al. (2012) did not found an effect of mulching on soil microbial biomass and activity at t=4 months. These results with burnt soils contrast with those with unburnt soils in which gross NO_3^- immobilisation was higher in the mulched soils than in the control ones (Cheng et al., 2012b), likely because straw increases C availability and enhances the activity of microbial communities responsible of NO_3^- immobilisation (Recous et al., 1990).

The evolution of NH_4^+ and NO_3^- concentrations in US suggests that there is no substrate limitation in this soil and that N mineralisation and nitrification could be sustained for a longer period. On the contrary, in burnt soils the shortage of available substrate for N mineralisation and the active nitrification would probably lead to increased NO_3^- levels until the NH_4^+ pool

is depleted. However, care must be taken when extrapolating these results and predictions to field conditions as soils preincubated in the laboratory might behave differently.

In general, forest ecosystems and undisturbed grasslands have a conservative N cycle with low net mineralisation and low autotrophic nitrification (Davidson et al., 1992). However, N additions and disturbance can alter this balance by stimulating autotrophic nitrification (Vitousek et al., 1979) and, if plant uptake does not increase, NO_3^- will probably be lost through leaching and denitrification (Stockdale et al., 2002). Similarly, burnt soils have large amounts of NH_4^+ due to combustion and high mineralisation rates, and plant uptake is negligible immediately after the fire. The relative dominance of the two main processes using NH_4^+ (O_{NH4} and I_{NH4}) has been suggested as a good indicator for potential N losses from soils (Stockdale et al., 2002). In the present study, the O_{NH4}/I_{NH4} ratio, was approximately 0.1 for all treatments at t=3 months and for US at t=6 months, while BS and BSM showed a much higher ratio (1.2) after 6 months of preincubation due to both the decrease in I_{NH4} and the increase in O_{NH4}. These results point to a significantly increased risk for N losses from the ecosystem after fire. As N losses in our laboratory experiment are low or nil, the NO_3^- pool sharply increased in the long-term preincubation, but in field conditions, if that amount of NO_3^- is produced, the potential risk of N losses would be high. Whether N losses through leaching or denitrification dominate in burnt soils is unknown, but emissions of the greenhouse gas nitrous oxide (N_2O) have been studied in burnt soils (Karhu et al., 2015). Available data shows either increased (Fierro and Castaldi, 2011; Karhu et al., 2015), negative or unaltered N_2O emissions due to fire (Anderson and Poth, 1998; Dannenmann et al., 2011; Inclán et al., 2012). In a laboratory experiment, Karhu et al. (2015) identified denitrification as the main source of N_2O in burnt soils, most probably due to the increased nitrification supplying NO_3^- (Castaldi and Aragosa, 2002; Karhu et al., 2015). The high N_2O emissions from burnt soils might not be recorded in the field due to drier conditions, but they could be triggered by heavy rains (Karhu et al., 2015).

To conclude, after 3 months of preincubation gross mineralisation and gross NH_4^+ immobilisation dominate in severely burnt soils; whereas after 6 months the soil N cycle opens up and NO_3^- accumulates in burnt soils, increasing the risk of N losses. Whether this is also the case in field conditions becomes paramount as it would have important consequences extending beyond the burnt ecosystem: N losses on-site, increased risk of eutrophication off-site and N_2O emissions due to denitrification. This study also shows that in laboratory conditions straw mulching application, very effective in reducing post-fire erosion, has no negative impact on gross N transformation rates and should be further investigated under field conditions.

6.4 Palmés experiment

6.4.1 Material and methods

6.4.1.1 Site description

Soils were collected from the area of Palmés wildfire (Galicia, NW Spain; UTM 29T $^{05}87$ $^{46}89$, Fig. 6.10) which took place in late July 2015 and burnt 230 ha of pine forest (*Pinus pinaster* and scattered individuals of *Ulex europaeus*). The burnt area is a.s.l. with a SE orientation and it lays on an adamellitic granite bedrock with a Dystric Leptosol (IUSS Working Group, 2014). Within a distance of 80-100 m from the burnt place, an unburnt area with the same topography, orientation, vegetation cover and soil type was identified as control for the experiment and sampled in a similar way.

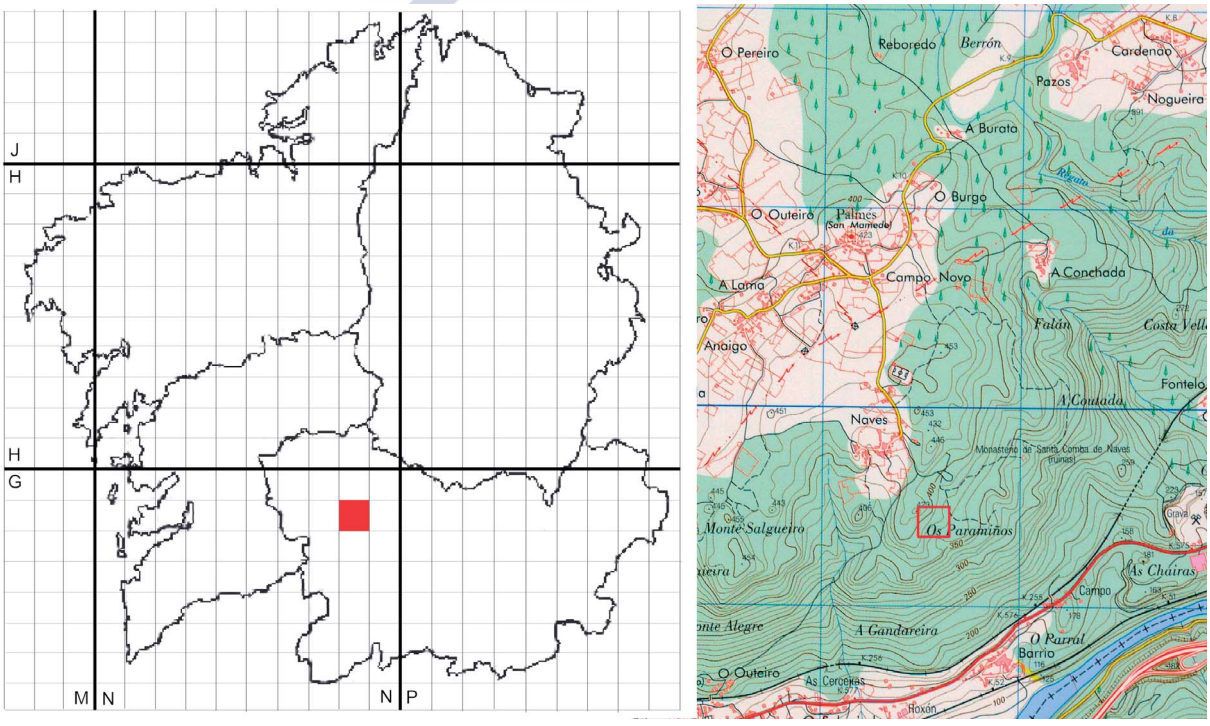

Figure 6.10: Location of the Palmés experimental field (red square) in the 10x10 km UTM grid map of Galicia (left) and in the topographic map (right).

6.4.1.2 Soil sampling

Top soil (0-2 cm depth) was sampled from the burnt and control areas within the first 3 days after burning. Two different kinds of burnt samples were taken: soil affected by burning with intermediate severity and soil affected by fire with high severity (Vega et al., 2013a). Samples were collected in several spots meeting the already stated burning severity requisites and combined into two composite samples. In the unburnt area, soil from 10 squares of 15x15 cm

were sampled and combined into a composite sample. The litter layer was sampled separately from the same 15x15 cm squares, air-dried and weighed to determine the amount of litter per surface area (2.2 kg m^{-2}). In the laboratory all the soils were sieved (< 2 mm) and homogenised. For the mulching treatments, wheat straw was harvested in an agricultural field located in the same region.

6.4.1.3 Soil, litter and straw characterisation

Soil subsamples were air-dried and finely ground (< 100 μm) in a planetary ball mill (Retsch PM100, Retsch GmbH, Haan, Germany, with cups and balls of zirconium oxide). The dry matter content of both fresh and air-dried soils was assessed by oven-drying sub-samples at 105 ℃ for 5 h. The water holding capacity (WHC) of fresh soils was determined in a Richards' membrane-plate extractor at a pressure of 10 kPa.

Soils were analysed for pH, SOC, SON and inorganic N immediately following sampling (t=0 months) and after each preincubation period (t=3 months and t=6 months). Soil pH was measured on air-dried samples with a pH meter (Metröhm, Switzerland) in KCl employing a 1:2.5 soil/solution ratio. Soil organic C and N were measured on ground samples with an elemental analyser (Carlo Erba CNS 1508). The method for quantifying soil content of NH_4^+ and NO_3^- is described in the following section. All analyses were carried out in duplicate (if the coefficient of variation was higher than 5% the analyses were repeated) and the mean of both analyses for each replicate was used.

6.4.1.4 Soil incubation and gross N transformation rates

An outdoor experiment was set up to assess how soil gross N transformation rates are affected by different burning severities and straw addition in weather conditions as close as possible to those in the field. Soils were preincubated in the garden of our institution (Santiago de Compostela) from the 10th November 2015 until the 12th February 2016 (113 days of preincubation, from now on referred as t=3 months) and until the 9th May 2016 (196 days of preincubation, from now on referred as t=6 months) within a fenced area which allowed soil samples to be exposed to weather conditions but prevented animals or litterfall to reach the soil trays. Precipitation and mean temperatures were recorded throughout the whole incubation period (Fig. 6.11). The soils were divided into five treatments: unburnt soil (US), intermediate severity burnt soil without (BI) and with mulching (BIM) and high severity burnt soil without (BH) and with straw mulching (BHM). Approximately 2000 g of wet soil per treatment were placed in two plastic trays of 20 x 20 x 2 cm (one tray for each preincubation time). For US, BIM and BHM, a piece of nylon mesh (1 mm^2 mesh size) was placed on top of the soil to facilitate the separation of litter and straw from the soil. On top of the unburnt controls, an equivalent amount of litter to that found in the field was added (2.2 kg m^{-2}). Both BIM and BHM received 250 g m^{-2} of straw, a frequently

used dose that ensures a soil cover higher than 60% and, thus, effectively reduces erosion. Five holes (5 mm diameter) per tray were done to allow drainage of percolating water.

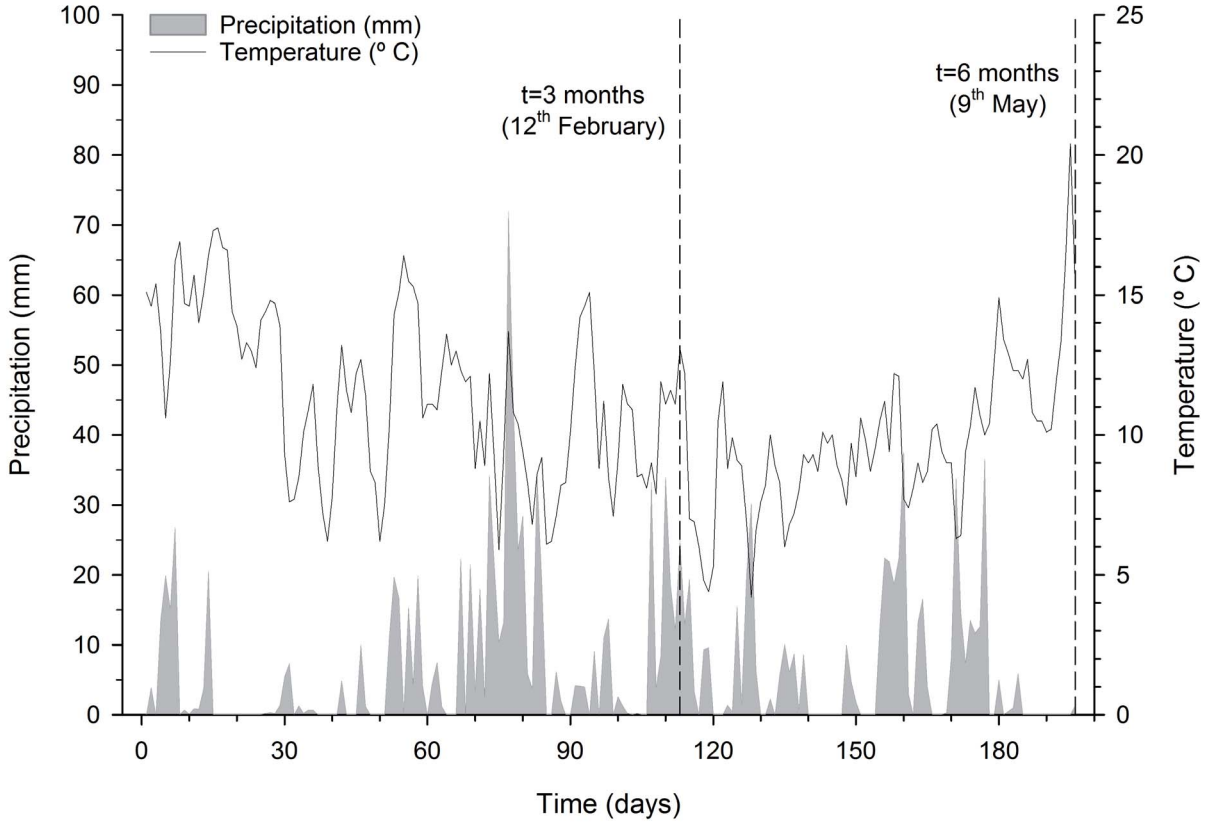

Figure 6.11: Daily precipitation (mm) and mean temperature (ºC) during the preincubation period.

After each preincubation period, soils were thoroughly homogenised and a paired ^{15}N labelling experiment, with $^{15}NH_4NO_3$ and $NH_4{}^{15}NO_3$ as tracers and five incubation times (0.5 h, 1, 3, 7 and 14 days), was conducted. Aliquots equivalent to of dry soil were placed in a total of 300 centrifuge bottles (250 ml): five treatments, two preincubation times, two ^{15}N-tracers, five incubation times and three replicates. The bottles were filled with 4 successive layers of soil, each of which received 1 ml of ^{15}N-tracer solution added uniformly over the soil surface with an automatic pipette (i.e. 4 ml per bottle). After a prior inorganic N quantification of the soil samples, several tracer solutions were prepared for the different treatments aiming to get the desired ^{15}N enrichment for the labelled samples without increasing too much the size of the measured N pool. The prepared tracer solutions were equivalent to a N addition of 0.5 to 3.5 mg kg^{-1} dry soil with a ^{15}N excess fraction of 20 to 98%. After labelling, soils were incubated in darkness at the mean air temperature during the preceding week, i.e. 9 ºC and 14 ºC for the 3 and 6 months preincubations, respectively. Once incubated, soils were thoroughly mixed and an aliquot of approximately was oven-dried at 105 ºC and finely ground

(<100 μm) for total N analyses. The rest of the labelled soil was extracted with 150 ml KCl 2M (1:5 soil:solution ratio) shaken for 1 h and passed through glass microfibre filters (Whatman GF/A, 125 mm diameter) for NH_4^+-N and NO_3^--N quantification with the extraction-diffusion method described in Couto-Vázquez and González-Prieto (2006), but at 55 ℃ instead of at room temperature. The $(NH_4)_2SO_4$ solutions resulting from NH_4^+ and NO_3^- titrations were evaporated to dryness in a vacuum oven (Memmert VO400, PM400) for obtaining $(NH_4)_2SO_4$ crystals. To accelerate the drying process, the oven was alternatively under vacuum (15 kPa) and atmospheric pressure. In order to trap possible traces of atmospheric NH_3, the incoming air was passed through a column of activated charcoal. The $(NH_4)_2SO_4$ crystals were finally packed into tin capsules for ^{15}N analyses. The ^{15}N enrichment of NH_4^+-N and NO_3^--N, as well as the total N content and its ^{15}N enrichment were measured with an elemental analyser (Carlo Erba CNS 1508) coupled on-line with an isotopic ratio mass spectrometer (Finnigan Mat, delta C, Bremen, Germany). An elemental reference material (Soil 3 from Eurovector, Milano, Italy) and an isotopic standard (IAEA-N1, IAEA-N2, IAEA 305-A, IAEA 305-B and IAEA 311, alternately, from the International Atomic Energy Agency, Vienna, Austria) were included in each set of 10 samples to check the accuracy of the results; if necessary, drift correction was made against internal standards during the run.

6.4.1.5 ^{15}N-tracing model

The ^{15}N tracing model *Ntrace* (Müller et al., 2007; Rütting and Müller, 2007) used in this experiment is one of the latest developments and allows a more complex description of the soil N processes as a large number of parameters can simultaneously be estimated (Rütting and Müller, 2007). It basically consists on a set of differential equations solved by numerical methods and non-linear fitting routines which search for rate parameters that minimize the misfit between modelled data and a set of observed data and avoid to be trapped in local minima (Rütting and Müller, 2007). The main differences between the gross rates we present here and those reported in other studies on burnt soils are: 1) we estimated gross autotrophic and heterotrophic nitrification separately; 2) we quantified immobilisation of NH_4^+ to SON and immobilisation of NO_3^- to SON separately; 3) we quantified dissimilatory nitrate reduction to NH_4^+ (DNRA) and denitrification; and 4) rates are estimated for the whole incubation period instead of sequentially.

To quantify gross N transformation rates for each of the treatments and preincubation times, a *Ntrace* compartment model with different N pools and possible N transformations was suggested as a start point. To identify the best option describing the measured data, the model was run several times changing the number of considered processes and the Akaike information criterion was used to choose the final model (Staelens et al., 2012). The parameters of the selected transformation rates were estimated using a Markov chain Monte Carlo (MCMC) method by fitting the model values to the measured contents and ^{15}N enrichments of NH_4^+ and NO_3^- (Müller et al., 2007). The optimisation procedure results in a probability density functions

(PDFs) from which parameter averages and standard deviations were calculated (Müller et al., 2007). For transformations following first order kinetics, average rates were calculated by integrating gross N rates over the experimental period divided by the total time (Rütting and Müller, 2007). Standard errors of means were calculated based on autocorrelation as described in Harmon and Challenor (1997). Statistically significance in differences between treatments was tested by an overlap of the 85% confidence intervals (CI) (Payton et al., 2000; Rütting et al., 2010). The ^{15}N tracing model is set up in Simulink (The Math Works Inc.) and it is summoned by the MCMC optimisation routine programmed in MatLab (The Math Works Inc.).

The N pools considered for the modelling were: exchangeable NH_4^+, adsorbed NH_4^+, NO_3^-, recalcitrant soil organic N (SONrec) and labile soil organic N (SONlab). In some soils, NH_4^+ can be instantaneously adsorbed after label addition, having important consequences for N dynamics. According to Münchmeyer (2001), we have inferred the amount of adsorbed NH_4^+ for each treatment considering the amounts of added and recovered ^{15}N. The compartmentalisation of SON in two pools, a microbially easily available fraction (SONlab) and a more difficult to mineralize fraction (SONrec), has been conceptually defined in some papers and it often helps to better model the mineralisation rate of SON (Müller et al. 2004; Nelissen et al. 2012). We have defined SON pools according to Nelissen et al. (2012): SONrec and SONlab accounted for 99% and 1% of the total SON, respectively. The initial pool sizes and ^{15}N abundance for NH_4^+ and NO_3^- as well as the initial total ^{15}N recovery were estimated by extrapolating back to t=0 the measurements from the first two soil extractions (t=0.5 hours and t=1 day) (Müller et al. 2004).

The following gross N transformations were initially considered in all the models: mineralisation of recalcitrant SON to NH_4^+ (M_{SONrec}), immobilisation of NH_4^+ to recalcitrant SON (I_{NH4rec}), mineralisation of labile SON to NH_4^+ (M_{SONlab}), immobilisation of NH_4^+ to labile SON (I_{NH4}), oxidation of SON to NO_3^- (heterotrophic nitrification, O_{SON}), immobilisation of NO_3^- to SON (I_{NO3}), oxidation of NH_4^+ to NO_3^- (autotrophic nitrification, O_{NH4}), dissimilatory nitrate reduction to ammonium (DNRA), denitrification (D_{NO3}), adsorption of NH_4^+ and desorption of NH_4^+. *Ntrace* is also able to model NH_3 volatilisation, but this rate was discarded due to the low soil pH. All transformations were described by first order kinetics, except M_{SONrec} and O_{SON} which followed zero order kinetics. If the values yielded by the model for a certain rate were close to 0, they did not follow a normal distribution and the inclusion of the rate did not improve the performance of the model, the rate was not retained in the model (Akaike information criterion). According to this, immobilisation of NH_4^+ to recalcitrant SON, adsorption of NH_4^+ and desorption of NH_4^+ were not considered in any of the modelled soils, being the other N rates retained at least in one of the soils.

6.4.2 Results

6.4.2.1 Soil pH, WHC, C and N content

Immediately after sampling (t=0 months), the WHC was 446 ± 20 g H_2O kg^{-1} dw in US samples and slightly higher for BI (481 ± 10 g H_2O kg^{-1} dw) and BH (513 ± 5 g H_2O kg^{-1} dw). The water content of the soils employed for ^{15}N tracer incubations was 1.8x (US), 1.2x (BI), 1.5x (BIM) and 1.1x (BH and BHM) the corresponding WHC at t= 3 months, and 1.5x (US), 1.3x (BI), 1.1x (BIM), 1.1x (BH) and 0.9x (BHM) at t= 6 months.

At t=0 months, unburnt soils had a pH_{KCl} of 2.96 ± 0.01 and burnt soils showed higher values increasing with burnt severity (3.61 ± 0.01 and 5.98 ± 0.04 for BI and BH respectively). During the preincubation, pH_{KCl} initially increased in US (3 months: 3.25 ± 0.02) and then remained stable (6 months: 3.23 ± 0.02). In the medium severity burnt soils, there was a transient increase of pH_{KCl} after 3 months (3.95-3.99) followed by a decrease after 6 months (3.75-3.78), while in the high severity burnt soils there was a sustained decrease down to 5.65-5.72 (t=3 months) and 5.07-5.25 (t=6 months).

Initially (t=0 months), total C was higher in BI (11.73 ± 0.03 mol kg^{-1} dw) and US (9.99 ± 0.24 mol kg^{-1} dw) than in BH (3.70 ± 0.06 mol kg^{-1} dw) and the total N content in US was 295 ± 2 mmol kg^{-1} dw, having BH almost the same amount (282 ± 4 mmol kg^{-1} dw) and BI 1.8 times more N (531 ± 5 mmol kg^{-1} dw). During the preincubations, total C and N content fluctuated within each treatment, but the differences between treatments remained similar (BI ≈ US > BH for C; BI > BH ≈ US for N). The C/N ratio (% total C/% total N) was higher in US (27-29) than in the moderately burnt soils (BI and BIM: 19-21) and highly burnt soils (BH and BHM: 11-13). Litter applied on top of US soils and straw applied on BIM and BHM treatments had, respectively, C/N ratios of 58 and 72.

Inorganic N content (NH_4^+-N + NO_3^--N) in US samples at t=0 months was 0.53 ± 0.04 mmol kg^{-1} dw, and it increased with time (2.4x at t=3 months and 3.4x at t= 6 months). On the contrary, the initial inorganic N content in BI and BIM (5.37 ± 0.02 mmol kg^{-1} dw) remained almost the same at t=3 months and decreased substantially at t=6 months (0.3x and 0.1x the initial values, respectively). Inorganic N content in BH and BHM (5.52 ± 0.13 mmol kg^{-1} dw at t=0 months) experienced an important decrease at t=3 months (0.3x and 0.2x the initial values, respectively) followed by a slight recovery at t=6 months (0.4x the initial values for both treatments). Initial inorganic N content in burnt soils was 10 times higher than in the unburnt control, but this difference substantially decreased during the preincubation. At t=3 months BI and BIM had 4-5 times more inorganic N than US soils, BH only had slightly higher values than the unburnt control (1.4 times higher) and inorganic N content in BHM was similar to US. After 6 months of preincubation, all treatments had similar inorganic N contents except BIM, which had approximately one third of this amount.

The content of NH_4^+-N also increased with time in US (0.53 ± 0.03 mmol kg^{-1} dw at t=0 months, 2.3x and 3.2x at t=3 and t=6 months, respectively) (Fig. 6.12). In BI the initial

NH_4^+-N content was 5.31 ± 0.01 mmol kg^{-1} dw, it remained similar at t=3 months and then dropped after 6 months of preincubation by a factor of 5 (BI) and 10 (BIM). For BH the initial content of NH_4^+-N was 5.52 ± 0.13 mmol kg^{-1} dw, at t=3 months a strong decrease (0.1-0.2x) was recorded and at t=6 months values remained similar in BH and slightly increased without reaching initial values in BHM. At t=0 months, NH_4^+-N accounted for 99% of the inorganic N in all treatments and thus differences in NH_4^+ content between treatments are the same as explained for inorganic N. While at t=3 months NH_4^+-N accounted for more than 90% of the inorganic N in US, BI and BIM, its importance decreased to 53-63% in BH and BHM; at t=6 months NH_4^+-N still accounted for 95% of the inorganic N in US, but the value decreased to 66-69% in BI and BIM and slightly increased to 68-78% in BH and BHM. Nonetheless, differences between treatments for the two preincubation times followed more or less the same pattern as described for inorganic N: at t=3 months burnt soils had more NH_4^+-N than the unburnt control (including BH and BHM, whose inorganic N content was lower than in US) and at t=6 months all treatments had approximately the same amount of NH_4^+-N except for BIM, which had around one fourth of this amount. The pool of adsorbed NH_4^+ is much smaller (0.06x) than the exchangeable NH_4^+ pool in all soils, except in BIM t=6 months (0.98x) and, to a lesser extent, in BHM t=3 months (0.24x) (Fig. 6.12).

The amount of NO_3^--N increased with time in all treatments (Fig. 6.12), being in general the magnitude of the change much greater than for inorganic N or NH_4^+-N because initial NO_3^--N levels were always below 0.06 mmol kg^{-1} dw. At t=3 months, the highest increase was recorded in BH and BHM (0.67 ± 0.31 and 0.57 ± 0.18 mmol kg^{-1} dw, respectively), followed by US, BI and BIM. After 6 months of preincubation, the NO_3^--N content doubled the t=3 months values in US and remained similar in the burnt soils. Compared with US, the NO_3^--N content in burnt soils was 5 (BIM) to 15 times higher (BI, BH and BHM) at t=3 months, being these differences reduced to 2 (BIM) and 6 times (BI, BH and BHM) at t=6 months.

The NH_4^+/NO_3^- ratio of soils at t=0 months was very high due to the extremely low NO_3^- content and they should be interpreted cautiously. After 3 months of preincubation, US had the highest NH_4^+/NO_3^- ratio (30.0), followed by BIM (22.4), BI (10.0), BH (1.7) and BHM (1.1); while at t= 6 months this ratio was substantially lower in US (18.9), BI (2.2) and BIM (1.9) and increased in BH (2.1) and BHM (3.5).

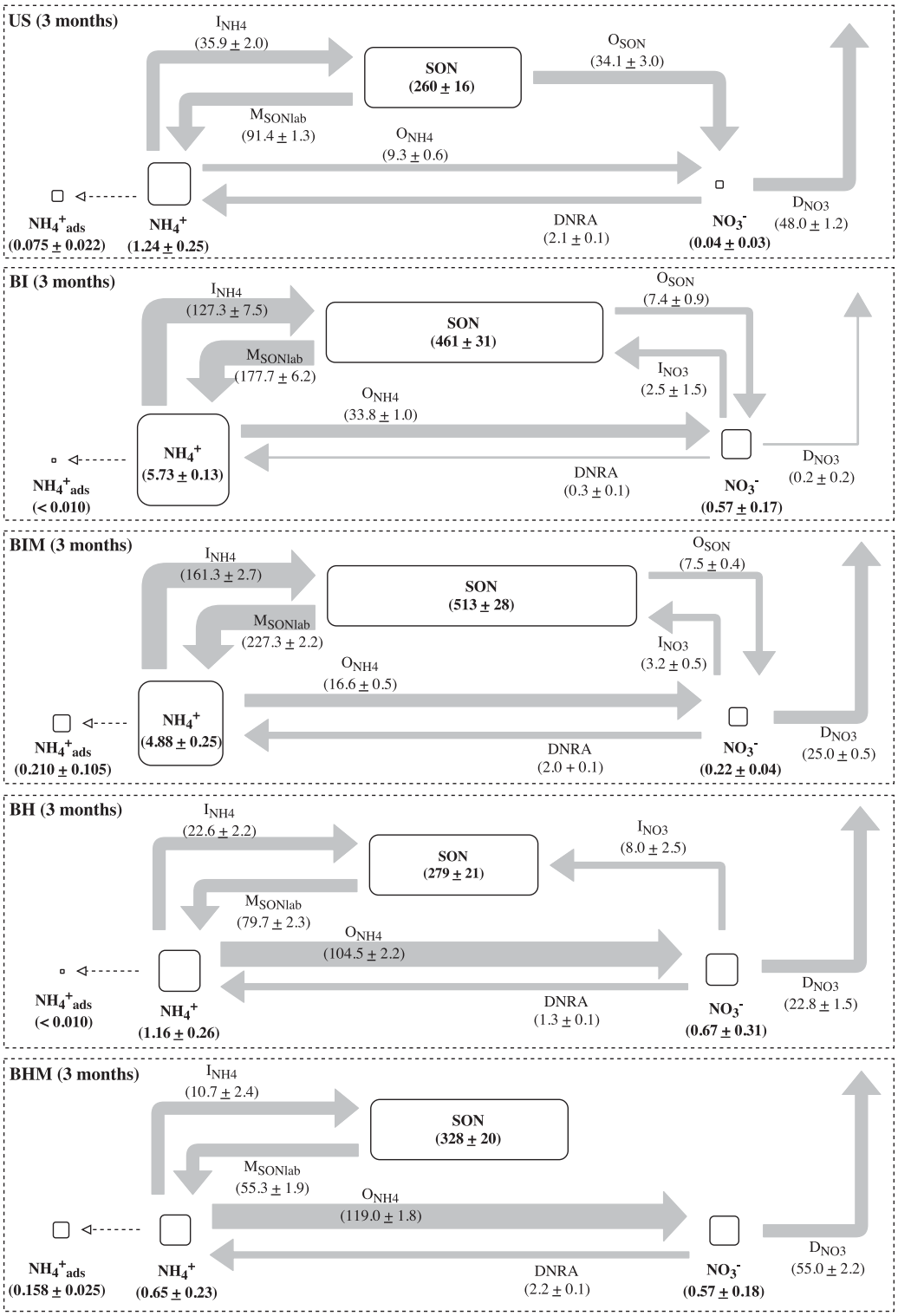

Figure 6.12: Gross N transformation rates (μmol N kg^{-1} dw day^{-1}; mean ± S.D.) and size of N pools (mmol N kg^{-1} dw; mean ± S.D.) for US, BI, BIM, BH and BHM after 3 and 6 months of preincubation. Box size is proportional to the N pool size (1:1) except for SON (1:40). To visually show the main differences among the rates, four arrow widths are defined according to increasing orders of magnitude (from 0.1 to 1000 μmol), but note that their width is not strictly proportional to the true rate values (included between brackets). (See key in the next page)

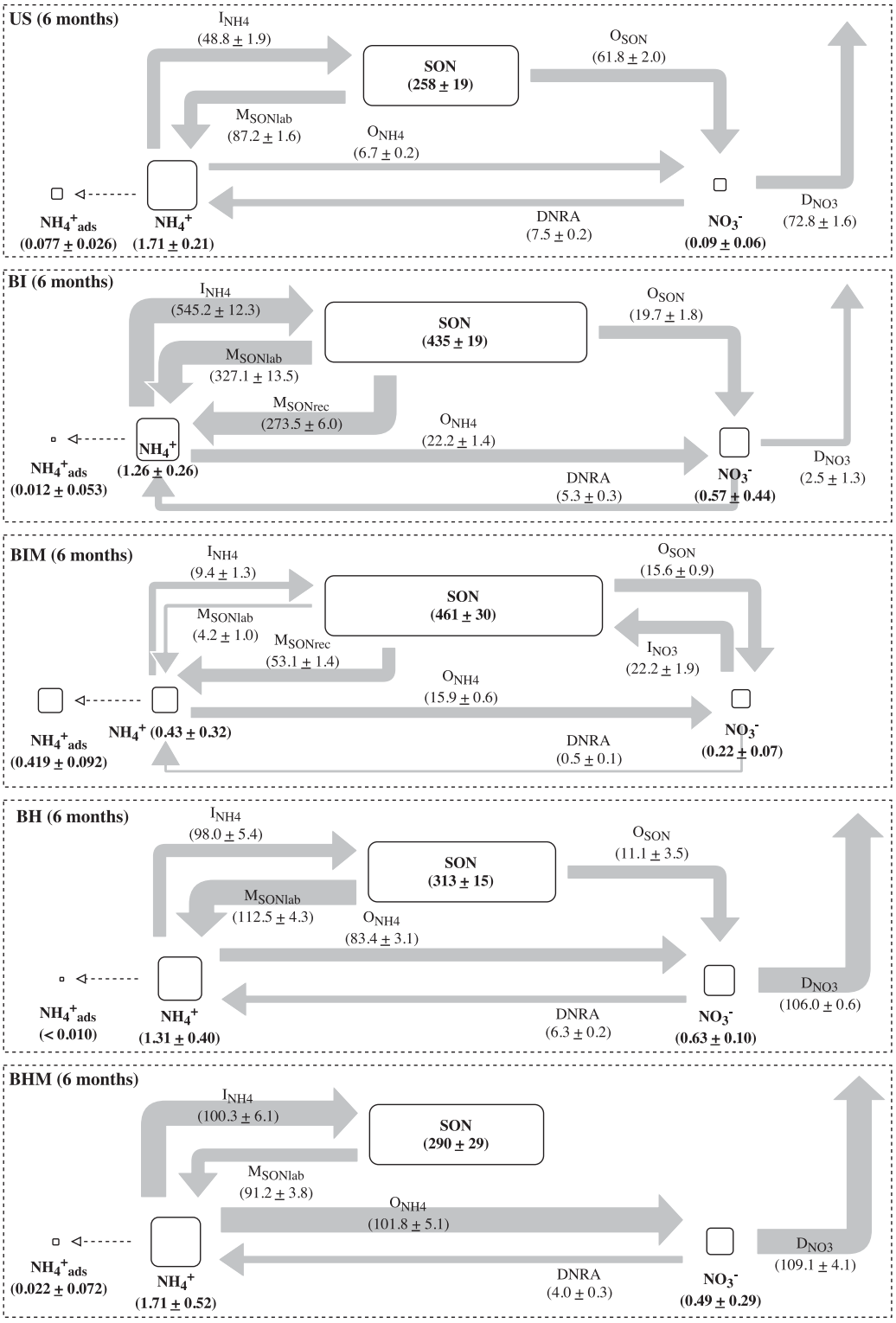

Figure 6.12 (cont.): Key: US, unburnt soil; BIM and BI, intermediate severity burnt soil with and without mulching, respectively; BHM and BH, high severity burnt soil with and without straw mulching, respectively; SON, soil organic N; M_{SONlab}, mineralisation of labile SON to NH_4^+; M_{SONrec}, mineralisation of recalcitrant SON to NH_4^+; I_{NH4}, immobilisation of NH_4^+ to labile SON; I_{NO3}, immobilisation of NO_3^- to SON; O_{SON}, heterotrophic nitrification or oxidation of SON to NO_3^-; O_{NH4}, autotrophic nitrification or oxidation of NH_4^+ to NO_3^-; DNRA, dissimilatory nitrate reduction to ammonium; and D_{NO3}, denitrification.

6.4.2.2 Gross N transformation rates

In general, the performance of the models was good (Table 6.1) and the distribution of the probability density functions of the estimated parameters had well defined normal distributions (data not shown). With some exceptions, there was a good fit between the output of the *Ntrace* model and the measured data (Figs. 6.13, 6.14, 6.15, 6.16, 6.17, 6.18, 6.19, 6.20, 6.21 and 6.22). The fitting between experimental and modelled NH_4^+ concentrations at the end of the tracer incubation (t=14 days) was not good at 6 months in BI and BIM (underestimation of experimental values), as well as at 3 and 6 months in BH and at 6 months in BHM (overestimation of experimental values). The measured NO_3^- concentrations were underestimated by the model at t=14 days in BIM (3 months) and BI (6 months). The modelled ^{15}N abundance in the NH_4^+ pool ($^{15}NH_4NO_3$ tracer) overestimated experimental values in the second half of BIM (6 months) incubation or around the middle of BHM (3 months) incubation. Similarly, the modelled ^{15}N abundance in the NO_3^- pool ($NH_4{}^{15}NO_3$ tracer) underestimated, to a variable degree, the experimental values in the second half of the incubations of most soils at t=3 months, but only in US at t=6 months. The experimental data for ^{15}N recovery was rather disperse in highly burnt soils at t=3 and 6 months; and at t=6 months the fitting of ^{15}N recovery was middling in US and bad in PBIM. According to the 85% overlap of the confidence intervals, all rate comparisons yielded significant differences.

All gross N transformation rates are expressed on a soil dry weight basis and presented in Fig. 6.12. For each N transformation rate, the difference between treatments and preincubation times was calculated considering as reference value the following: a) t=3 months when comparing the rate of each treatment between the two preincubation times; b) US when assessing the effect of fire; c) BI and BIM when testing fire severity effects on unmulched and mulched samples, respectively; and d) BI and BH when assessing the effect of mulching on medium and highly burnt soils, respectively. For each gross N transformation rate, all differences tested (by an overlap of the 85% CI) were significant both between treatments (same preincubation time) and between preincubation times (same treatment).

Table 6.1: Performance of the final models for each soil (misfit function, acceptance and number of iterations). Key: US, unburnt soil; BIM and BI, intermediate severity burnt soil with and without mulching, respectively; BHM and BH, high severity burnt soil with and without straw mulching, respectively.

	3 months			6 months		
	misfit	acceptance	iterations	misfit	acceptance	iterations
US	11086	46%	50000	1256	49%	50000
BI	3317	85%	150000	868	53%	80000
BIM	2386	56%	150000	6577	81%	80000
BH	861	39%	50000	442	33%	100000
BHM	912	55%	50000	779	71%	50000

The rate of labile SON mineralisation to NH_4^+ (M_{SONlab}) at t=3 months in US was 91.4 ± 1.3 μmol N kg^{-1} dw day^{-1}. Compared to US values, medium severity burning had a positive effect on this rate (1.9x in BI; 2.5x in BIM), but high severity burning caused a reduction of M_{SONlab} (0.9x in BH; 0.6x in BHM). Straw mulching had contrasting effects depending on fire severity: while mulching enhanced M_{SONlab} in moderately burnt soils (BIM: 1.3x BI) it reduced this rate in highly burnt soils (BHM: 0.7x BH). Increasing fire severity reduced M_{SONlab} both in unmulched (BH: 0.4x BI) and mulched (BHM: 0.2x BIM) soils. Compared to t=3 months, M_{SONlab} at t=6 months remained almost the same in US, decreased in BIM (0.02x) and increased in the other treatments: 1.8x (BI), 1.4x (BH) and 1.6x (BHM). Therefore, compared to US, M_{SONlab} in burnt soils at t=6 months was higher in BI (3.8x) and BH (1.3x), similar in BHM (1.0x) and lower in BIM (0.05x). The positive effect of straw on M_{SONlab} in medium severity burnt soils recorded at t=3 months turned into a negative effect at t=6 months (BIM: 0.01x BI); while in high severity burnt soils there was still a negative effect of mulching although of lesser magnitude (BHM: 0.8x BH). Only BI and BIM (t=6 months) presented M_{SONrec} (273.5 ± 6.0 and 53.1 ± 1.4 μmol N kg^{-1} dw day^{-1}, respectively). When both SON mineralisation rates are considered together for these soils, the positive effect of fire on the rate was even greater in BI (M_{SONrec} + M_{SONlab} was 6.9x M_{SONlab} in US), and was not as negative in BIM (M_{SONrec} + M_{SONlab} was 0.7x M_{SONlab} in US).

Immobilisation of NH_4^+ to labile SON (I_{NH4}), followed a similar pattern to M_{SONlab}. After 3 months of preincubation, I_{NH4} in US was 35.9 ± 2.0 μmol N kg^{-1} dw day^{-1}, less than half of M_{SONlab}. Taking US as reference, I_{NH4} was higher in moderately burnt soils (3.5x in BI; 4.5x in BIM), but lower in highly burnt soils I_{NH4} (0.6x in BH; 0.3x in BHM). Straw addition enhanced I_{NH4} in moderately burnt soils (BIM: 1.3x BI), but depressed this rate in highly burnt soils (BHM: 0.5x BH). As for M_{SONlab}, increasing fire severity reduced I_{NH4} both in unmulched (BH: 0.2x BI) and mulched soils (BHM: 0.1x BIM). At t=6 months, I_{NH4} decreased in BIM (0.06x) compared to t= 3 months, but it increased in US (1.4x) and especially in the other treatments: 4.3x in BI and BH; and 9.4x in BHM. As a result, compared to US, at t=6 months I_{NH4} was much higher in BI (11.2x) and to a lesser extent in BH and BHM (2.1x), but lower in BIM (0.2x). At t=6 months straw had no longer a negative effect on I_{NH4} in the severely burnt soils (BHM ≈ BH), and its positive effect recorded at t=3 months for the medium severity burnt soils was reverted (BIM: 0.02x BI).

Heterotrophic nitrification (O_{SON}) in US at t=3 months was 34.1 ± 3.0 μmol N kg^{-1} dw day^{-1}, around one third of M_{SONlab}. Our final *Ntrace* model did not retain O_{SON} for the severely burnt soils (BH and BHM), while in medium severity burnt soils this rate was only 0.2x that in US. After 6 months of preincubation, O_{SON} was retained in all soils except BHM, and compared to the corresponding values at t=3 months, the rate was 1.8x in US, 2.7x in BI and 2.1x in BIM. Therefore, at t=6 months O_{SON} in burnt soils was lower than in US (0.3x in BI and BIM; 0.2x in BH).

At t=3 months, immobilisation of NO_3^- (I_{NO3}) was not modelled for US, and it was rather low in BI and BIM (2.5 to 3.2 μmol N kg^{-1} dw day^{-1}) and BH (8.0 ± 2.5 μmol N kg^{-1} dw day^{-1}); whereas at t=6 months, it was only included in BIM (22.2 ± 1.9 μmol N kg^{-1} dw day^{-1}).

Autotrophic nitrification (O_{NH4}) at t=3 months was low in US (9.3 ± 0.6 μmol N kg^{-1} dw day^{-1}) and increased with fire severity in the burnt soils (3.6x in BI, 1.8x in BIM, 11.2x in BH and 12.8 in BHM). Straw mulching slightly enhanced O_{NH4} in highly burnt soils (BHM: 1.1x BH) and quite the opposite in moderately burnt soils (BIM: 0.5x BI). At t=6 months the O_{NH4} rate remained similar in BIM and slightly decreased in the other soils compared to the respective t=3 months values (0.7x in US and BI, 0.8x in BH and 0.9x in BHM). Therefore, at t=6 months O_{NH4} was, compared to US values, greater in BH (12.4x) and BHM (15.2x) and, to a lesser extent, in BI (3.3x) and BIM (2.4x); and mulching also had a slight positive effect on O_{NH4} in highly burnt soils (BHM: 1.2x BH), but a slight negative effect in moderately burnt soils (BIM: 0.7x BI).

After 3 months of preincubation, the rate of dissimilatory nitrate reduction to ammonium (DNRA) in US was 2.1 ± 0.1 μmol N kg^{-1} dw day^{-1}, having similar values BIM and BHM and lower values BI (0.2x) and BH (0.6x). Straw had a positive effect on the rate in both moderately burnt soils (BIM: 6.1x BI) and highly burnt soils (BHM: 1.7x BH). At t=6 months, DNRA decreased in BIM (0.3x) and increased in the other soils: US (3.5x), BI (16.2x), BH (4.7x) and BHM (1.8x). Therefore, at t=6 months DNRA in burnt soils was 0.7x (BI), 0.1x (BIM), 0.8x (BH) and 0.5x (BHM) lower than in US; and straw mulching had a negative effect on this rate (BIM: 0.1x BI; and BHM: 0.6x BH).

At t=3 months denitrification (D_{NO3}) in US was (48.0 ± 1.2 μmol N kg^{-1} dw day^{-1}), only surpassed by BHM (1.1x) and having the other treatments much lower values than US (BIM and BH 0.5x) and BI almost no denitrification (0.2 ± 0.2 μmol N kg^{-1} dw day^{-1}). Straw mulching caused a substantial increase on denitrification in both highly and moderately burnt soils. After 6 months of preincubation, denitrification increased in US (1.5x), BI (10.5x), BH (4.7x) and BHM (2.0x), and was not retained in BIM. This lead to a positive effect of high severity burning on the rate (BH and BHM: 1.5x US), a negative effect of medium severity burning (BI: 0.03x US) and almost no effect of straw.

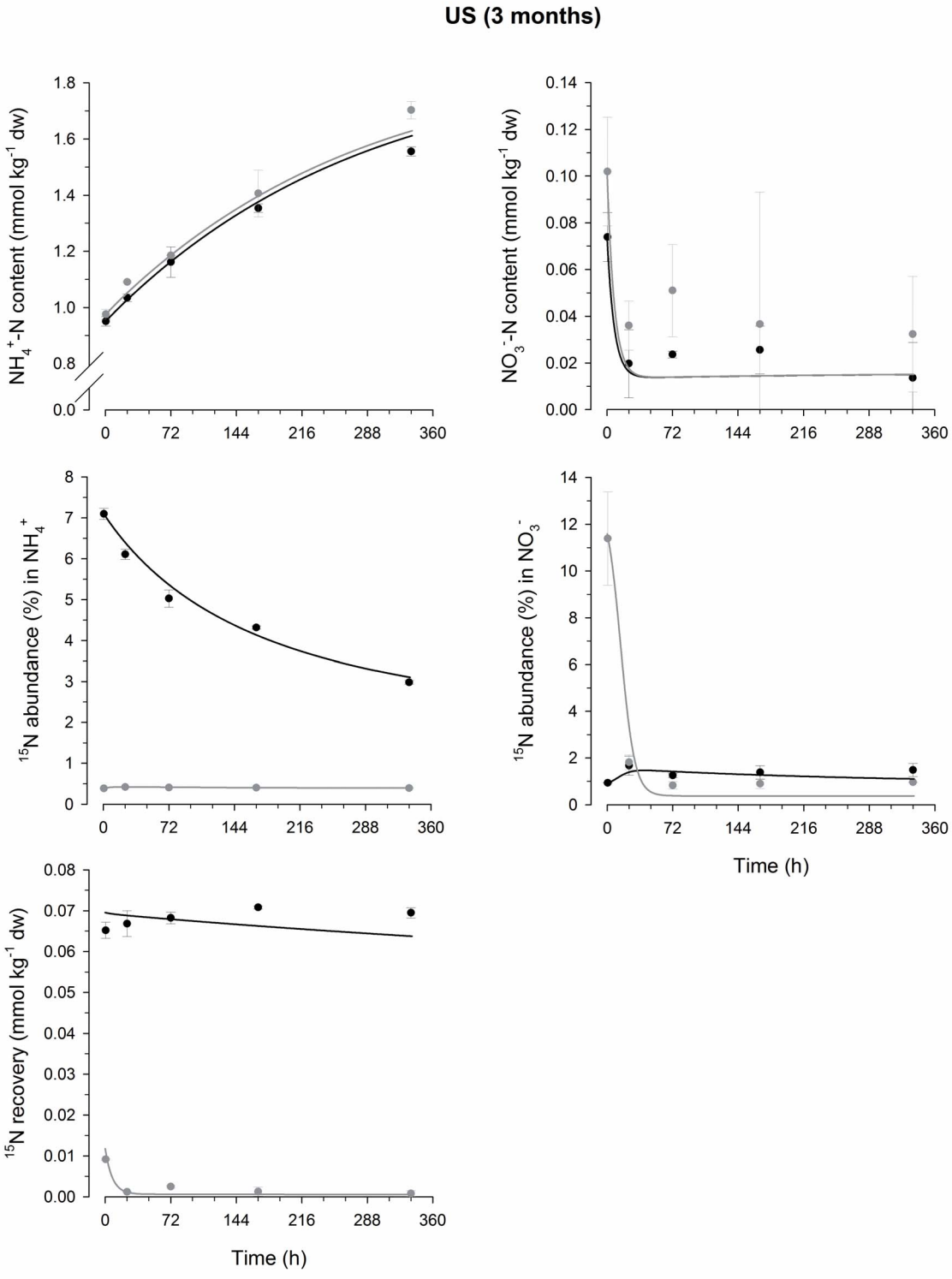

Figure 6.13: Model fit for the unburnt soil (US) at t=3 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

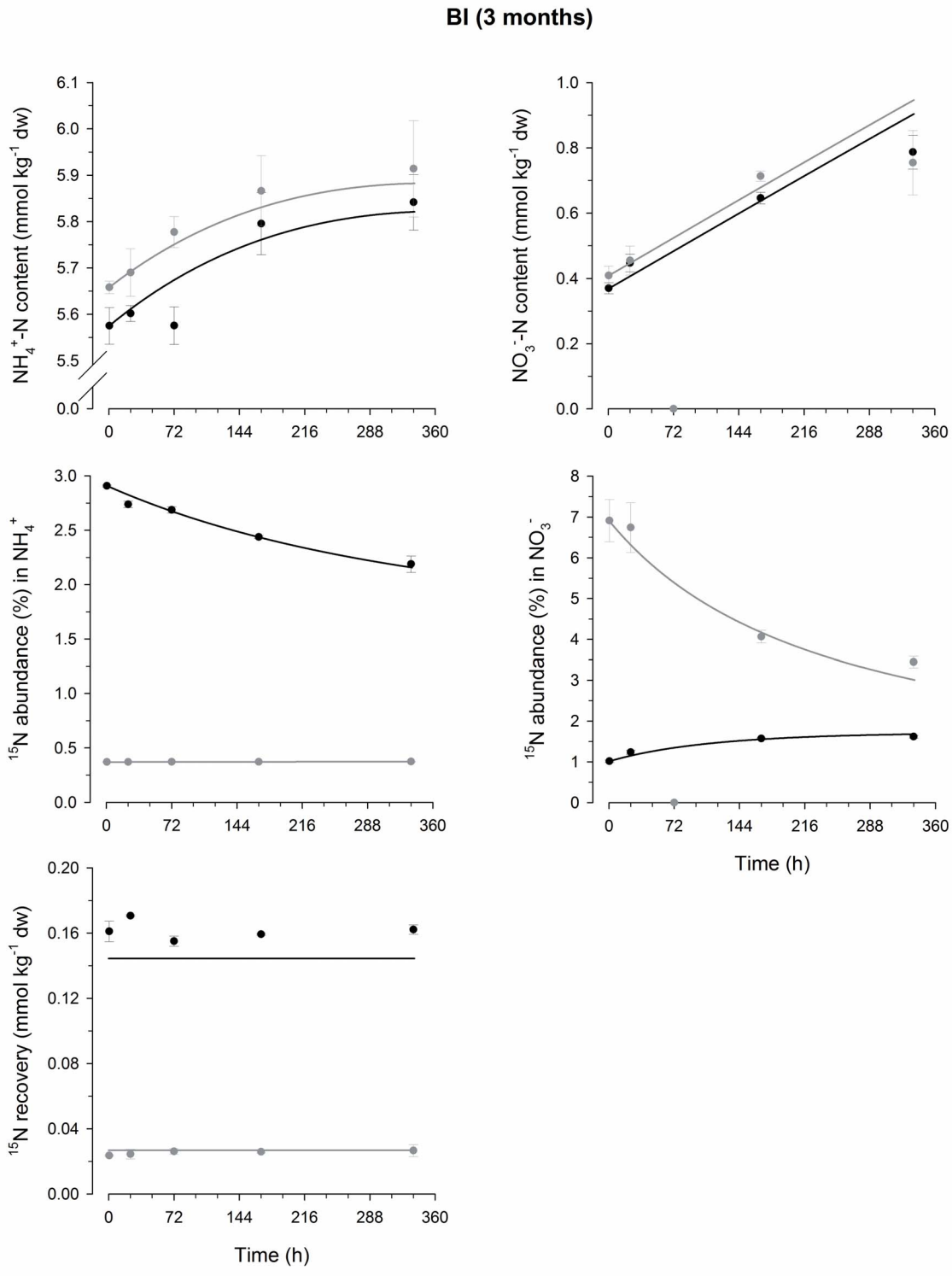

Figure 6.14: Model fit for the moderately burnt soil without mulching (BI) at t=3 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

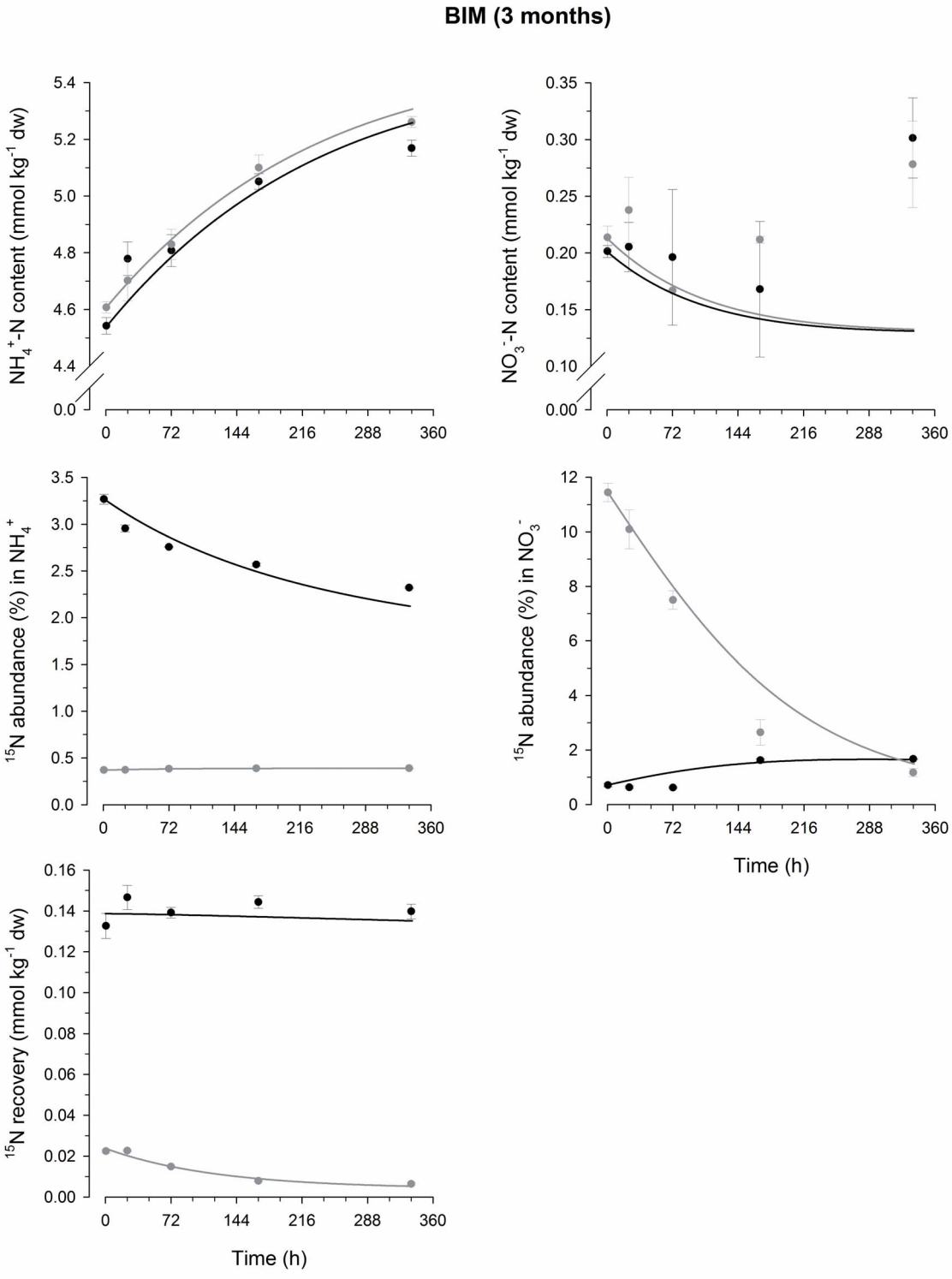

Figure 6.15: Model fit for the moderately burnt soil with mulching (BIM) at t=3 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

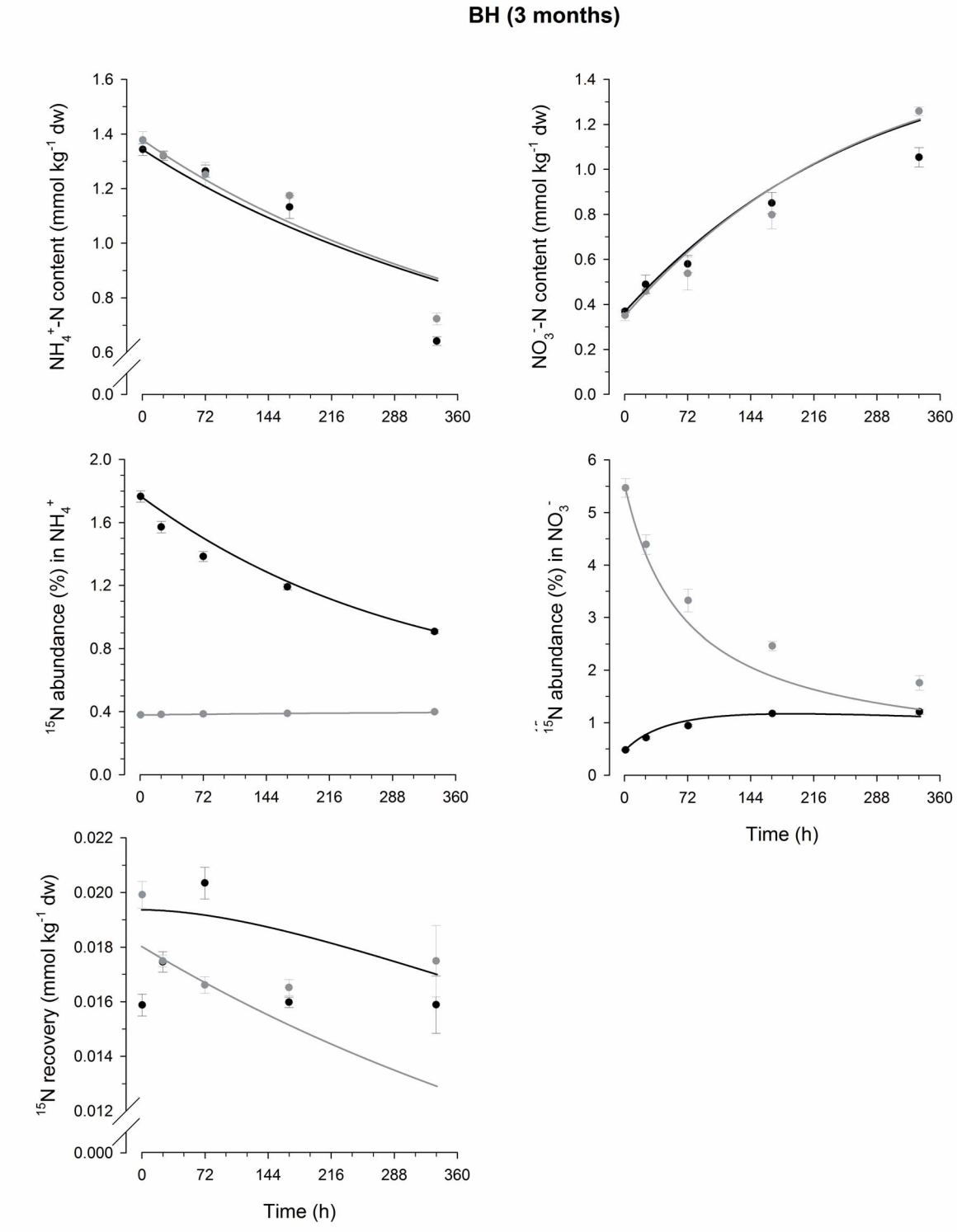

Figure 6.16: Model fit for the highly burnt soil without mulching (BH) at t=3 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

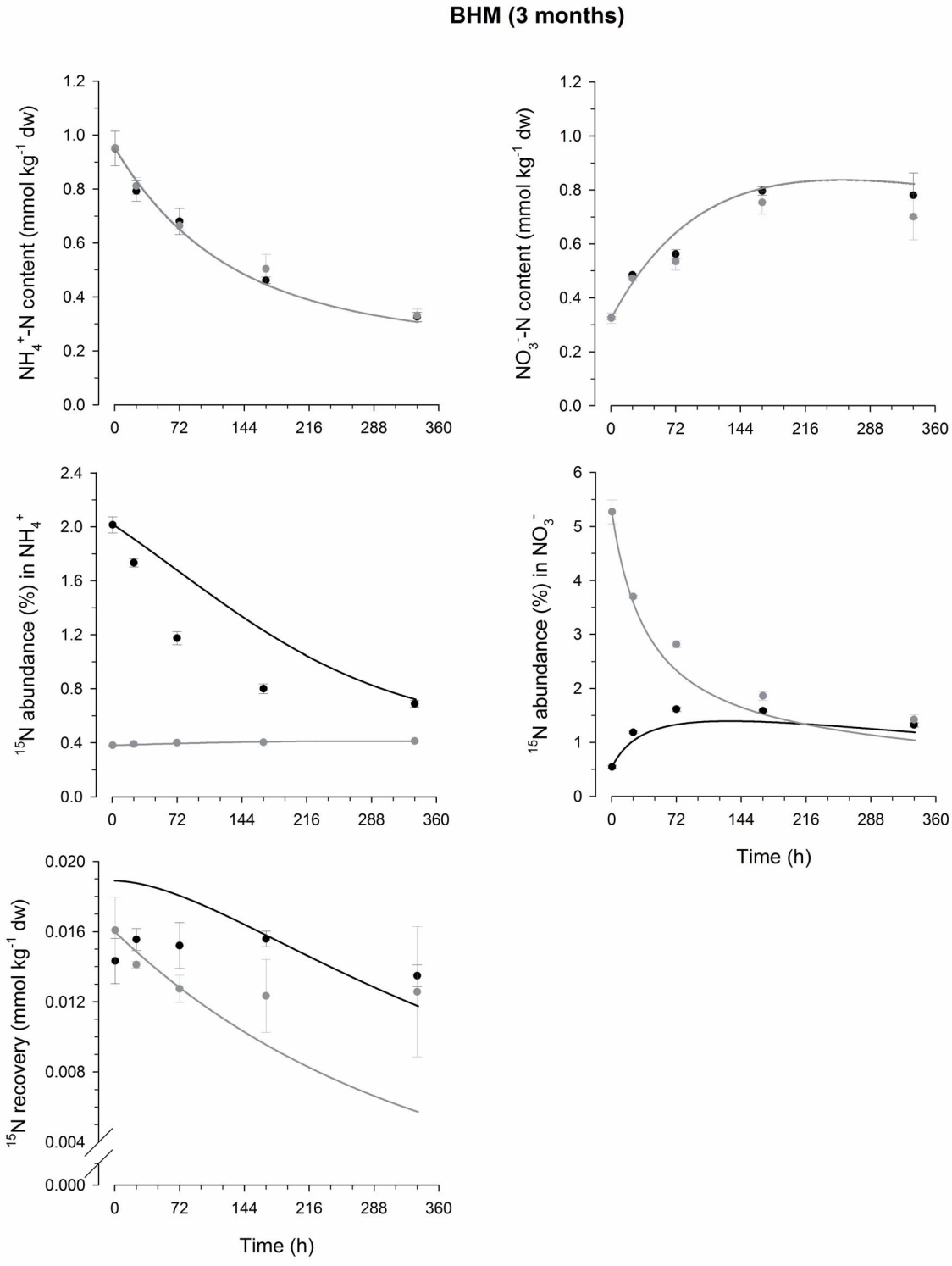

Figure 6.17: Model fit for the highly burnt soil with mulching (BHM) at t=3 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

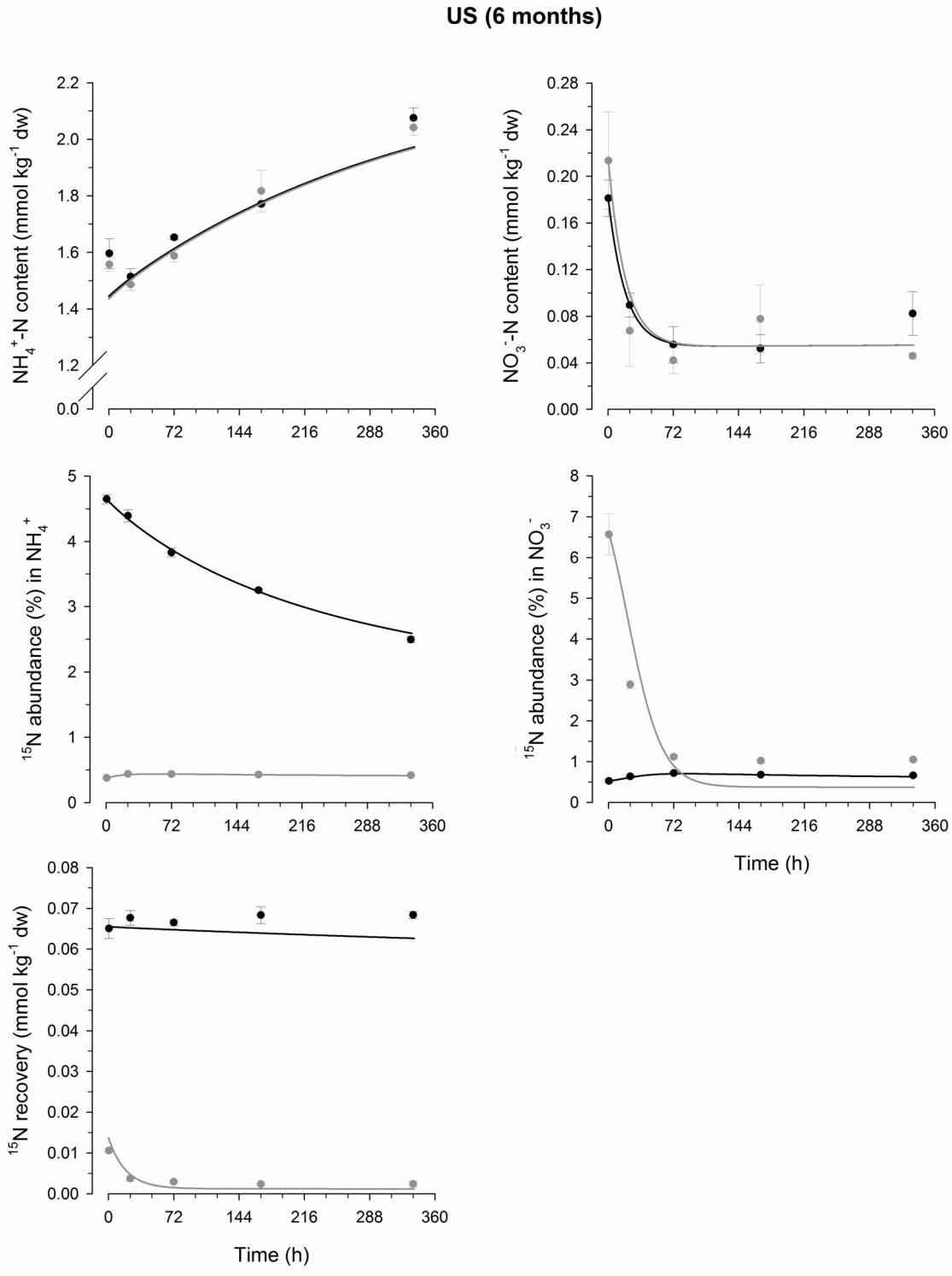

Figure 6.18: Model fit for the unburnt soil (US) at t=6 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

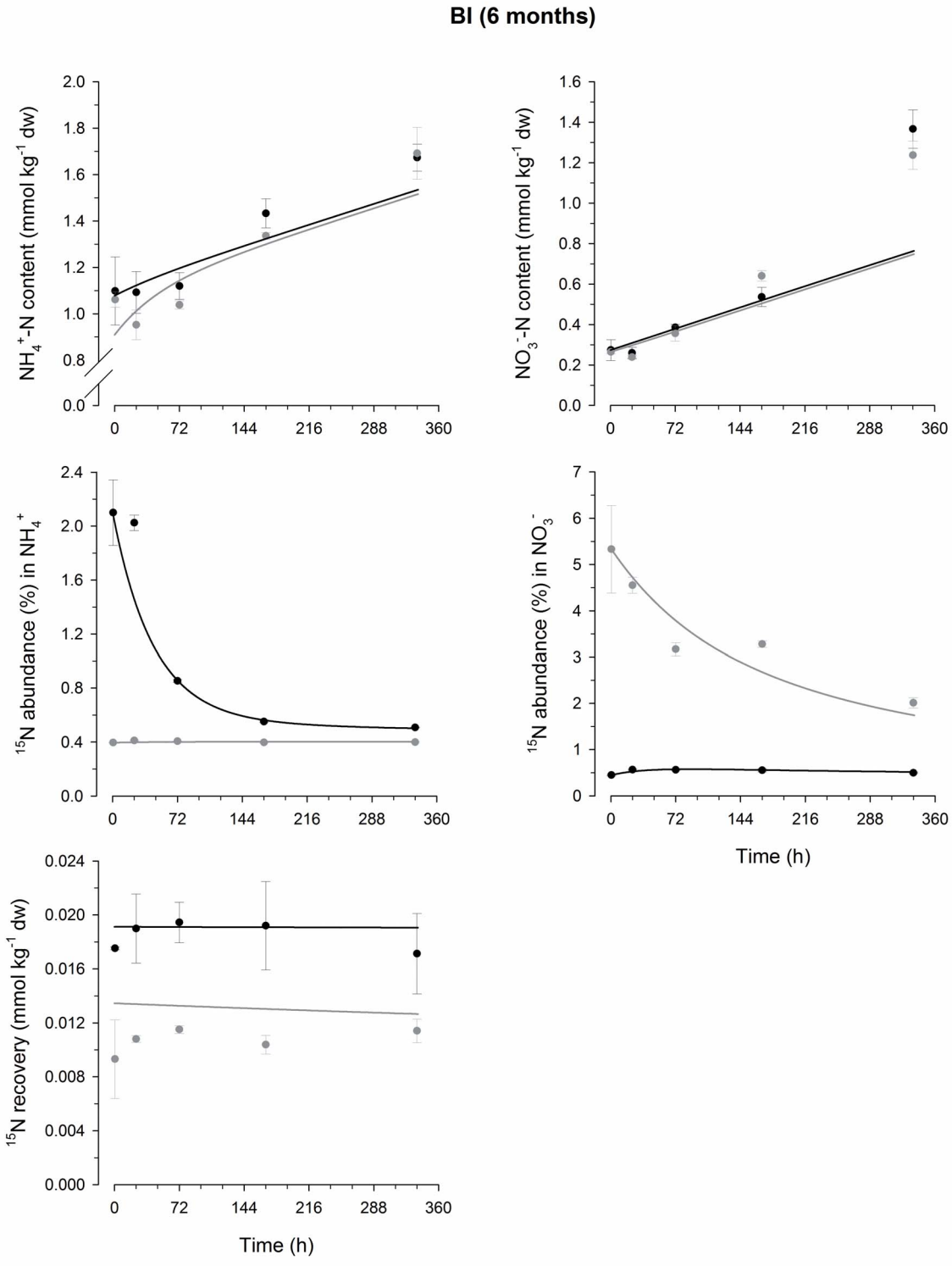

Figure 6.19: Model fit for the moderately burnt soil without mulching (BI) at t=6 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

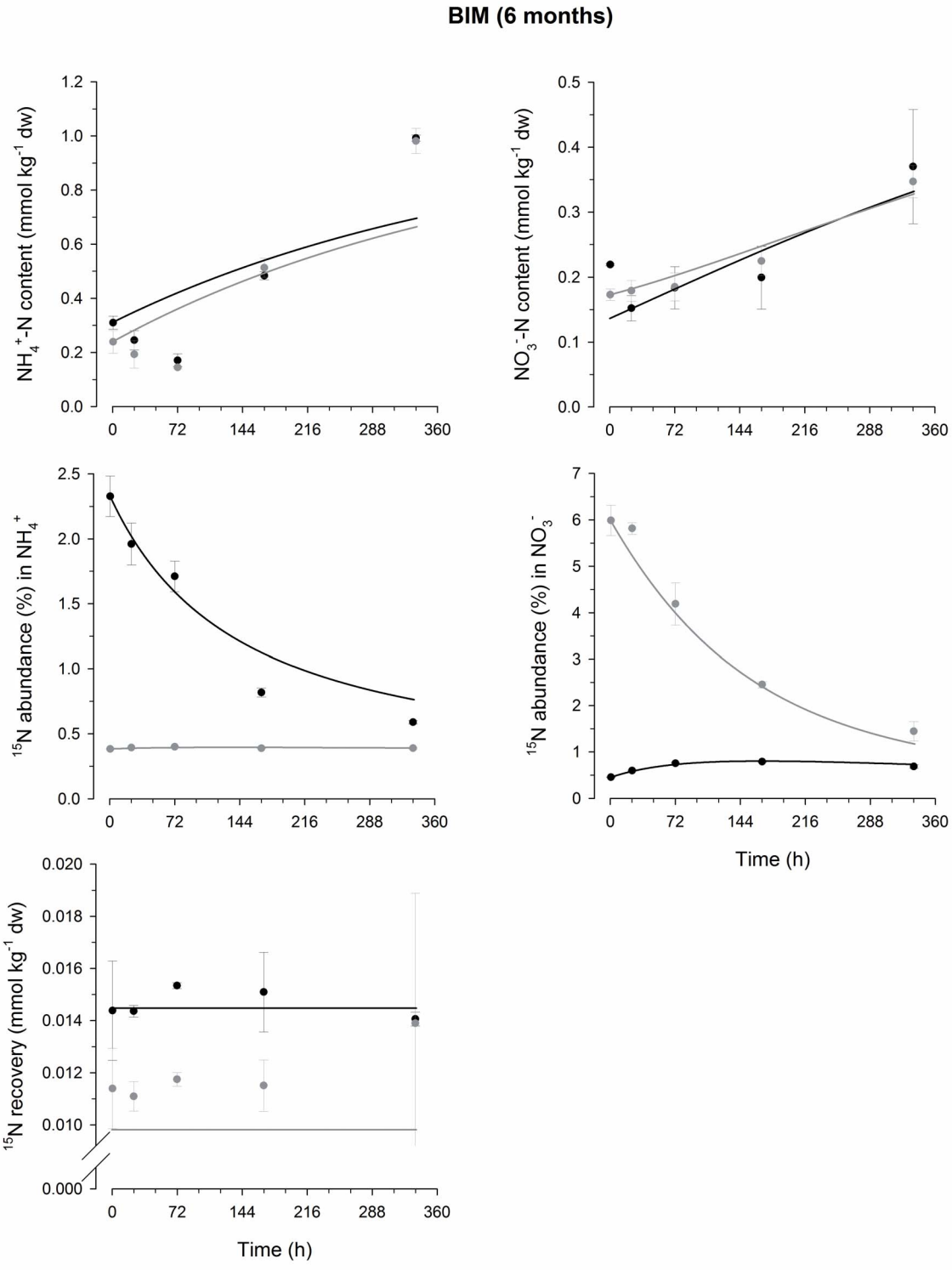

Figure 6.20: Model fit for the moderately burnt soil with mulching (BIM) at t=6 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

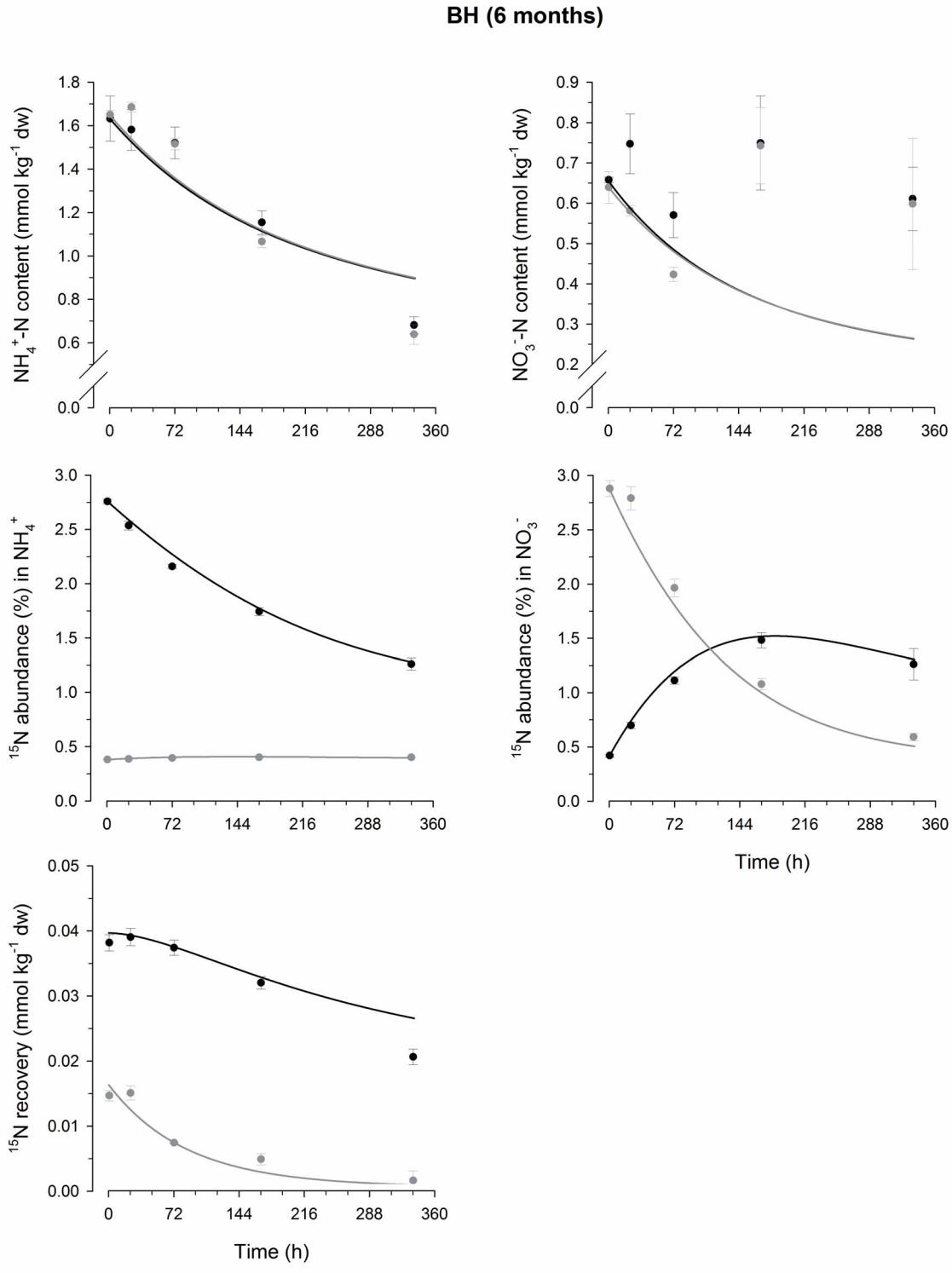

Figure 6.21: Model fit for the highly burnt soil without mulching (BH) at t=6 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

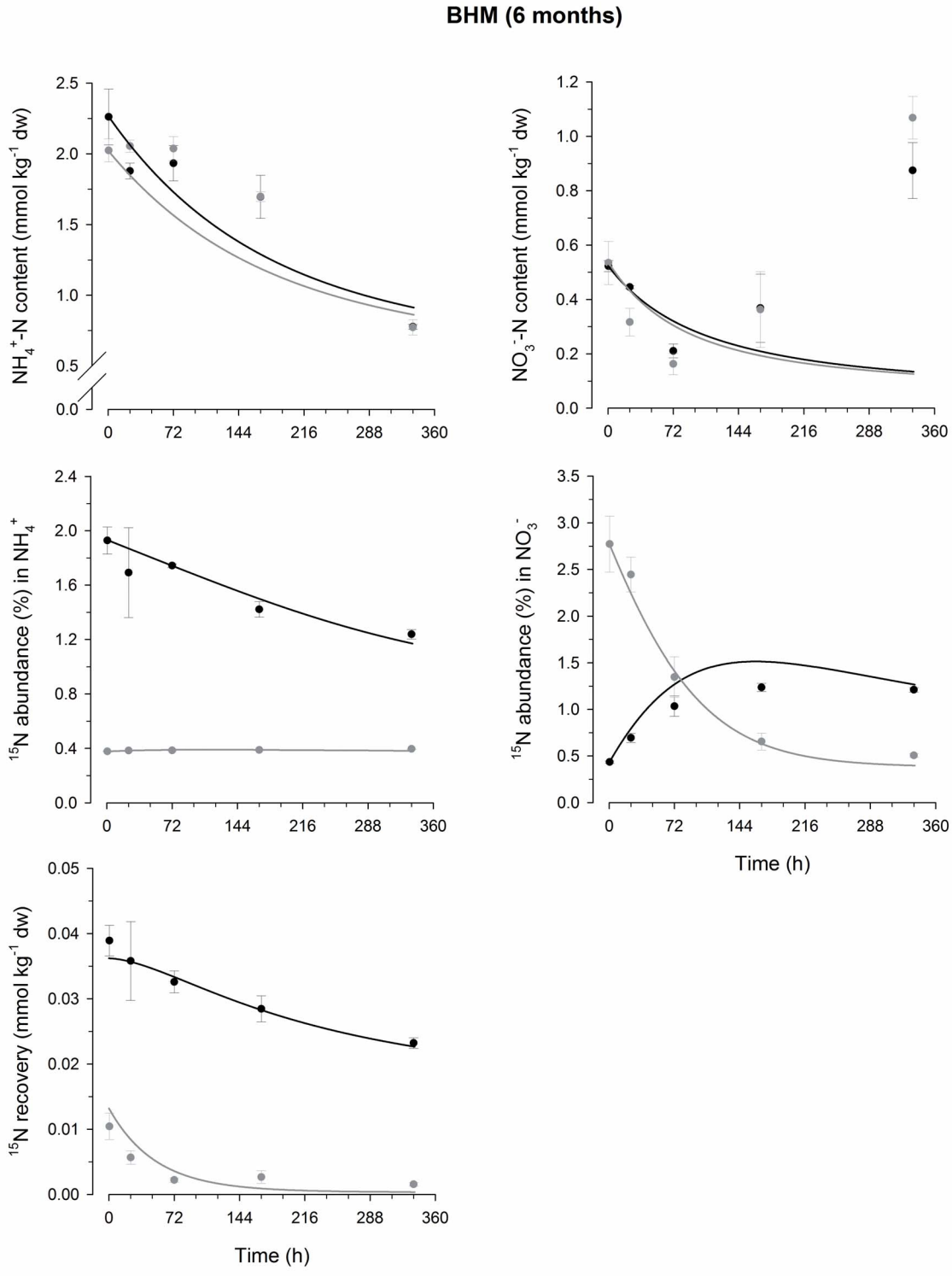

Figure 6.22: Model fit for the highly burnt soil with mulching (BHM) at t=6 months. Symbols represent measured concentrations of NH_4^+-N and NO_3^--N, the ^{15}N abundance in NH_4^+ and NO_3^- pools and the total ^{15}N recovery (mean ± S.D.), and modelled data is shown with lines. Black stands for incubations with $^{15}NH_4NO_3$ and grey for incubations with $NH_4{}^{15}NO_3$.

6.4.3 Discussion

Although the main aim of this experiment is to unravel fire and mulching effects on soil N rates, the chosen experimental set up superimposes variability on some important factors controlling N dynamics and, thus, it is sometimes complicated to elucidate whether fire and mulching themselves or rather the effects they produce on certain soil properties are behind the observed changes in gross N rates. Besides, if results from different studies dealing with gross N rates are compared among them, great attention should be paid to the conditions chosen for the incubations (temperature, humidity, laboratory or in situ experiments, etc.), as that could largely determine the observed differences in gross N rates.

Between the two preincubation times of the current experiment, there were several differences that must be highlighted (Fig. 6.12). The temperature increased from 9 ℃ (t=3 months) to 14 ℃ (t=6 months), and accumulated precipitation in the preceding week decreased substantially (from 110.1 to 1.3 mm). Another important difference between 3 and 6 months of preincubation was plant cover and height: while plants were ever absent in US (maybe due to the thick litter layer) and BH, they appeared at t= 6 months in the other treatments, being small in BI and tall and dense in the mulched plots (BHM and, especially, BIM), likely due to the seeds supplied with the straw mulch and to the better conditions for seed germination and growth.

Burning itself has a great impact on SOM quantity and quality, soil inorganic N, pH and WHC (Certini, 2005; Neary et al., 2008), ranging fire effects on SOM content from almost total destruction to substantial increases of it (González-Pérez et al., 2004). In this experiment, total C and total N were the highest in moderately burnt soils due to the partial combustion of vegetation and the incorporation of charred material and ashes into the soil, whereas highly burnt soils showed the lowest total C and N values, being C more strongly depleted than N as already reported in other studies (see González-Pérez et al. (2004) and references therein). Accordingly, the C/N ratio was the highest in US and decreased with burning severity as in González-Pérez et al. (2004), indicating that not only SOM quantity but also its quality was affected by burning. Inorganic N (especially NH_4^+) was higher in burnt soils as in other experiments (Couto-Vázquez and González-Prieto, 2006; Gómez-Rey et al., 2013a; Gómez-Rey and González-Prieto, 2014), but in US inorganic N content steadily increased during the preincubation while in burnt soils the final values were lower than the initial ones. The NH_4^+/NO_3^- ratio was above 15 in US in both preincubation times, decreased substantially with time in moderately burnt soils (BI, from 10 to 2; BIM, from 22 to 2) and was always below 4 in highly burnt soils. The decrease in total inorganic N concentrations together with the evolution of the NH_4^+/NO_3^- ratio is most probably indicating that during the preincubation period the burnt soils (especially BH and BHM) were more prone to N losses. The different extent of organic matter consumption might partly explain the reported pH differences: as plant material and organic matter were combusted, the amount of exchangeable cations increased and the pH as well (Certini, 2005). Although other studies report negative effects of fire on the WHC (Certini, 2005; Neary et al., 2008), in this experiment increasing burning severity positively affected the WHC. Moderately

burnt soils had the highest SOM content and, as WHC greatly depends on SOM, that may explain the high WHC of these soils. Conversely, highly burnt soils had the lowest SOM content but the highest WHC, being a possible reason the contribution of the clay fraction to soil water retention capacity. Clays are supposed to be quite resistant to burning (Neary et al., 2008), but information about how different clays are affected by fire is rather scarce and suggests that clay morphology and agglomeration are significantly changed by heating (Chen et al., 2016). Two different mechanisms, not mutually excluding, could explain the WHC increase in highly burnt soils: a) the high temperatures reached during Palmés fire might have greatly altered clay properties increasing their water retention capacity; or b) if the clay fraction was the main contributor to water retention capacity in Palmés soil, the combustion of a great proportion of SOM in the highly burnt soils could result in an increase of the relative importance of the clay fraction in the bulk soil and consequently in increased WHC. To sum up, US soils were always more saturated with water than burnt soils; and as the precipitation decreased substantially from t=3 months to t=6 months, soil moisture decreased in all treatments but BH.

The fitting between measured and modelled values showed that the calculated gross N fluxes were correct in most cases, being nitrification (either autotrophic or heterotrophic) the rate with the least conclusive data due to a risk of overestimation which was more frequent at t=3 months (US, BI, BH and BHM) than at t=6 months (only BI). In a few cases there was also a risk of overestimation of DNRA or I_{NO3} (BI 3 months and BIM 6 months), I_{NH4} (BH 6 months) and denitrification (BHM 6 months), while there was only one case of suspected underestimation (M_{SON} or M_{NREC} in BIM 6 months). The estimation of adsorbed NH_4^+-N, done according to Münchmeyer (2001) showed that this pool of abiotically fixed N was relatively small (except in BIM 6 months) and inactive, but that its inclusion in the *Ntrace* models significantly improved the model performance. Several publications explain the main factors controlling the N cycle in terrestrial ecosystems, being substrate content, temperature and soil moisture (itself and as regulator of O_2 supply and diffusion of other molecules) crucial environmental variables influencing soil microbial processes (Bengtson et al., 2005; Booth et al., 2005; Chen et al., 2015; Cheng et al., 2012a; Cheng et al., 2015). It is assumed that the factors controlling inorganic N assimilation (NH_4^+ and NO_3^- immobilisation) are similar to those regulating SON mineralisation as the microbial biomass as a whole is involved in these two counterbalancing processes (Booth et al., 2005), and they will be further discuss together and referred to as mineralisation-immobilisation turnover (MIT). The MIT is positively correlated with soil temperature, soil moisture and SON concentration, although SON quality also influences it and the effects of moisture and SON are difficult to separate because SOM content greatly determines the soil WHC (Booth et al., 2005). In general, microorganisms immobilize NH_4^+ rather than NO_3^- (see Booth et al. (2005) and references therein); in fact, NO_3^- immobilisation seems to be suppressed when NH_4^+ concentrations are high and it tends to be more frequent in microsites where NH_4^+ has been depleted (Chen and Stark, 2000). As soil sieving and homogenisation can greatly affect quantification of NO_3^- immobilisation due to microsite disruption (Booth et al., 2005), it is hard to interpret whether I_{NO3} is affected by the

chosen treatments or if it is rather a side effect of sample processing. Besides, I_{NO3} is usually very low in most soils and thus it is difficult to get normal distributions of this rate parameters with the *Ntrace* model (Tobias Rütting, personal communication). Autotrophic nitrifying bacteria are poor competitors for NH_4^+ (Robertson and Groffman, 2015), they are more sensitive to moisture and aeration status than most heterotrophic bacteria and fungi (Booth et al., 2005), and it seems that low pH exerts a negative influence on autotrophic nitrification in some soils (see Chen et al. (2015) and references therein). Heterotrophic nitrification is not linked to cellular growth and it is carried out by a wide range of microorganisms (De Boer and Kowalchuk, 2001). Although it is still under debate, some studies highlight the importance of heterotrophic nitrification in acid and organic matter rich soils, being the results contradictory about their relationship with precipitation and humidity (see Chen et al. (2015)). Dissimilatory nitrate reduction to ammonium (DNRA) is more common in soils than it was initially thought and, when moisture content is high, it seems to be an important process that can compete with denitrification (Chen et al., 2015; Rütting et al., 2011). Unfortunately, the factors regulating DNRA are not completely clear yet, although it seems that both climatic (temperature and precipitation) and edaphic (C and NO_3^- content) variables play an important role (Rütting et al., 2011). Biological denitrification is carried out by a wide range of microorganisms, but it only takes place when O_2 levels in the soil atmosphere decrease below a critical level of 11-14% either due to a shortage in O_2 supply (i.e. after rainfall in unsaturated soils) or to a high O_2 consumption by an intense heterotrophic activity (for example after organic amendments) (Firestone, 1982; Robertson and Groffman, 2015). Some studies report that DNRA is less sensitive to variable redox conditions and O_2 levels than denitrification, and that the available C/NO_3^- ratio (electron donor/acceptor ratio) determines whether NO_3^- undergoes denitrification or DNRA (see Rütting et al. (2011) and references therein).

Taking all these regulating mechanisms into account, our results suggest that, for Palmés soils, changes in overall heterotrophic activity (M_{SON}, O_{SON}, I_{NH4} and I_{NO3}) can be explained by the incubation temperature (3 months vs 6 months experiments) and the differences in SOM quantity and quality between the different soils. As during the incubations all soils from Palmés had a high moisture content (above their WHC), and thus O_2 availability in microsites might be limited, we hypothesize that those processes strongly regulated by O_2 supply are in the end controlled to some extent by heterotrophic activity because it is continuously depleting O_2. Therefore, high heterotrophic activity would have a negative influence on autotrophic nitrification and a positive effect on DNRA and denitrification. Nonetheless, the heterogeneous spatial distribution of substrate availability and O_2 supply in the soil greatly influences microbial activity and, thus, gross N rates.

In unburnt soils after 3 months of preincubation, mineralisation of labile SON, NH_4^+ immobilisation, heterotrophic nitrification and denitrification were one order of magnitude higher than autotrophic nitrification and DNRA. The low O_{NH4} rate might be explained by the comparatively higher MIT and the subsequent competition for NH_4^+ (Robertson and Groffman, 2015), as well as by the low O_2 levels due to both high soil moisture and heterotrophic activity.

The higher temperature at t=6 months might explain the higher I_{NH4} and O_{SON} rates (Booth et al., 2005). Similarly, DNRA increased substantially and denitrification almost doubled from 3 to 6 months, whereas autotrophic nitrifiers slightly decreased their activity despite the higher temperatures, most certainly due to the O_2 depletion by heterotrophs and a higher competence for NH_4^+ with NH_4^+ immobilizers.

After 3 months of preincubation, highly burnt soils had a lower MIT than US and there was not heterotrophic nitrification, most probably because the combustion process greatly affected the microbial community and also modified the SON so it was no longer easily available for the surviving heterotrophic microorganisms. As already discussed in the first part of this section, both positive and negative effects of fire on MIT have been reported and no clear conclusion can be drawn because there is a wide range of factors influencing MIT (fire severity, time since fire, method for rate estimations...) that cannot be disentangled with the few experiments done on the topic (Anderson and Poth, 1998; Bastias et al., 2006; Gómez-Rey and González-Prieto, 2013; Gómez-Rey and González-Prieto, 2015; Karhu et al., 2015; Neill et al., 1999). Conversely, autotrophic nitrification in highly burnt soils was the highest rate, as suggested in previous literature which states that ecosystem disturbances resulting in increased NH_4^+ availability (e.g. fires) usually promote nitrification (Robertson and Groffman, 2015; Vitousek et al., 1979). Moreover, the lower activity of heterotrophs and the concomitant increase in available O_2 might have also favoured autotrophic nitrifiers. In fact, the decrease in overall heterotrophic activity was more pronounced in BHM, soil that showed the highest autotrophic nitrification rate, although the fitting of experimental and modelled data suggests that autotrophic nitrification might be slightly overestimated in both highly burnt soils (Figs. 6.16 and 6.17). Denitrification in BHM was around 2 times higher than in BH, although heterotrophic activity was slightly higher in BH. This difference could be explained by net nitrification ((O_{NH4} + O_{SON}) – (I_{NO3} + DNRA)), which in BH accounted for 95 μmol N kg^{-1} dw day^{-1} and was higher in BHM (117 μmol N kg^{-1} dw day^{-1}), suggesting that denitrifiers had more readily available substrate in the latter. Moreover, the O_{NH4}/I_{NH4} ratio, also used as an indicator of potential NO_3^- losses from the system (Stockdale et al., 2002), was higher in BH (5) and BHM (11) (and both values were the highest for the whole experiment), supporting the higher denitrification rate found in BHM compared to BH and possibly anticipating the high denitrification rates reported 3 months later. Nonetheless, the fitting of experimental and modelled data suggests that denitrification might be slightly overestimated in BHM.

The observed changes in gross N rates at t=6 months in highly burnt soils (increase of MIT and denitrification, heterotrophic nitrification appeared in BH and slight decrease of autotrophic nitrification) were probably related with the higher temperatures and lower soil moisture. We hypothesize that the increasing temperature, and to a lower extent the availability of fresh labile compounds supplied by the growing plants in BHM, allowed MIT to speed up and thus autotrophic nitrifiers' growth was limited (by increasing competition for the substrate and reducing O_2 levels in microsites). Even though soil moisture at t=6 months was lower than at t=3 months (at least in BHM), the combination of higher temperatures and O_2 depletion in

microsites due to heterotrophic activity seem to be relevant enough to promote denitrification and DNRA, rates that also increased at t=6 months. It is noteworthy that highly burnt soils at t=6 months presented the highest denitrification rates of the whole experiment. Nevertheless, the much lower O_{NH4}/I_{NO3} ratio (0.9-1.0) suggests that this high denitrification rate might not be sustained much longer.

Moderately burnt soils, at t=3 months, had a substantially higher MIT compared to US due to the higher SOM content of these soils provided by charred plant material and ashes. Conversely, O_{SON} was lower in BI and BIM, although at least the rate was retained by the model (not the case in BH and BHM). It seems that burning exerts a negative effect on heterotrophic nitrifiers in Palmés soils, although in the Vilameá experiment O_{SON} was only detected in the burnt soils regardless preincubation time. There is no clear explanation for these contrasting results which could be due to the different conditions of both experiments (temperature, humidity and legacy effects of growing plants during the preincubation). As suggested for BH and BHM, the higher O_{NH4} in moderately burnt soils compared to the unburnt control can be a result of the disturbance caused by fire and the subsequent increase in available NH_4^+ together with the lower soil moisture. Furthermore, the high heterotrophic activity reported in moderately burnt soils (and the subsequent O_2 limitation in microsites) might be the reason why autotrophic nitrification in BI and BIM was not as high as in BH and BHM. Nevertheless, as stated before, O_{NH4} in BH and BHM might be overestimated and the diverse effects that increasing fire severity can have on SOM and microbial community should also be taken into account. Medium severity burning and straw mulching had contrasting effects on the denitrification rate, showing both BI and BIM lower D_{NO3} than US. Although net nitrification was higher in BI (38 μmol N kg^{-1} dw day^{-1}) than in BIM (19 μmol N kg^{-1} dw day^{-1}), denitrification in BI was almost zero and BIM presented a denitrification rate of similar magnitude to the other soils, most certainly indicating that the high heterotrophic activity of this soils promoted denitrification through low O_2 availability in soil microsites. Although straw mulching did not have a positive effect on MIT in highly burnt soils (probably because the microbial community was still recovering from the severe fire in both soils), in moderately burnt soils MIT was higher in BIM than in BI. As straw mulching supplies organic C and N, enhanced MIT rates have been reported in studies dealing both with unburnt (Huang et al., 2008; Shindo and Nishio, 2005; Watkins and Barraclough, 1996) and burnt soils (Gómez-Rey and González-Prieto, 2015).

After 6 months of preincubation, BI and BIM soils evolved in different directions. Whereas in BI the pattern was similar to BH and BHM (increase in MIT, O_{SON}, DNRA and denitrification, and reduction of O_{NH4}) and can be explained by the same mechanisms, in BIM the MIT decreased substantially, denitrification was absent, DNRA decreased and O_{SON} and I_{NO3} increased. Moreover, the legacy effects of plants and a new rate, mineralisation of recalcitrant SON, appeared in both moderately burnt soils, being the size of the plants higher in BIM and the magnitude of M_{SONrec} higher in BI. These differences between both soils, which were not recorded at t=3 months, might be a combined consequence of medium severity burning, straw application and plant growth. At t=3 months, when plants were absent in all treatments, the

main differences between highly and moderately burnt soils in the N cycle were driven by the amount and quality of SOM, and the role of straw as protective cover for the soil to provide suitable conditions for microbial growth and to avoid SOM losses seemed to be more important in moderately burnt soils. Conversely, three months later, plant establishment in certain soils and differences in their growth (BIM > BI > BHM) due to the combined effects of fire severity and straw, was probably the main factor shaping the soil N cycle. The large plants present in BIM were probably competing with microorganisms for available N and other nutrients, and providing root exudates able to down-regulate some of the microbially-mediated N transformation rates (Dannenmann et al., 2011). Nonetheless, great care should be taken when interpreting these results, because the fitting of experimental and modelled data (Figs. 6.19 and 6.20) suggest that I_{NH4} might be overestimated in BI, and M_{SONlab} and/or M_{SONrec} might be underestimated in BIM. Surprisingly, despite the literature stating that denitrification is usually enhanced by plants (due to root exudates and O_2 consumption, see Rütting et al. (2011) and references therein), no denitrification was modelled in BIM. The not so good fitting of total ^{15}N recovery probably indicates that the chosen model was not able to correctly estimate the denitrification rate.

In general, the experimental design and the methods usually employed to estimate gross N rates in soils do not allow to estimate autotrophic and heterotrophic nitrification independently (Barraclough and Puri, 1995). Therefore, as done with the results from Vilameá fire, total gross nitrification was calculated for Palmés soils in order to compare the results with data from other experiments. At t=3 months total gross nitrification in US was 43 μmol N kg^{-1} dw day^{-1}, and fire had contrasting effects on this rate: whereas it was 1.5 times higher in highly burnt soils, it was similar to US in BI but only half in BIM. At t=6 months, total gross nitrification slightly increased in US (1.6x) but remained rather similar in burnt soils. This study expands the knowledge about fire effects on gross nitrification, which up to date is quite contradictory with studies showing either no effect of burning on gross nitrification (Aranibar et al., 2003; Kaye and Hart, 1998; Neill et al., 1999), a positive effect (Vilameá experiment and Dannenmann et al. (2011)), or even inhibition of the rate (Gómez-Rey and González-Prieto, 2013; Gómez-Rey and González-Prieto, 2015). Therefore, it seems that increasing fire severity might be positively correlated with total gross nitrification and the consequences of that on N losses and greenhouse gas production in the context of climate change should not be disregarded (Karhu et al., 2015; Niboyet et al., 2011).

As far as we know, none of the previous studies dealing with gross N transformation rates in burnt soils considered DNRA, and denitrification has been mostly investigated by measuring gas fluxes (Dannenmann et al., 2011; Fierro and Castaldi, 2011; Inclán et al., 2012; Karhu et al., 2015). Until recently, most ^{15}N labelling experiments did not take DNRA into account because it was assumed to be negligible and its quantification with analytical models requires a mirror labelling approach, complicating the experimental design (Rütting et al., 2011). With the development of more advanced numerical methods, such as the model *Ntrace* we used, DNRA became to be considered in more studies and it seems that this rate is more common in soils

than previously thought (Rütting et al., 2011). In some soils DNRA is the dominant NO_3^- consumption process (Huygens et al., 2007; Rütting and Müller, 2008), and, for the first time, we reported it in a burnt soil and with a similar magnitude to that in the unburnt control. At t=3 months DNRA was the lowest rate in all Palmés soils but, likely due to the warmer temperature, three months later it increased substantially in all treatments except in BIM, where plants were the largest. The legacy effects of plant growth might have influenced DNRA in this soil, although plant interactions with DNRA are not well understood (Rütting et al., 2011). As fire often leads to a higher risk of N losses due to several reasons (vegetative cover absent, altered soil structure, higher O_{NH4}/I_{NH4} ratio), it would be interesting to assess the contribution of DNRA as a pathway for reducing N losses because NH_4^+ is less prone than NO_3^- to be lost from the soil. Moreover, the consequences of NO_3^- reduction partitioning between DNRA and denitrification goes beyond N retention within the soil system and have important implications for climate change because, even though DNRA can be a source of N_2O (see Rütting et al. (2011) and references therein), denitrification is the major source of N_2O emissions (Robertson and Groffman, 2015).

Both increased N_2O emissions following fire (Castaldi et al., 2010; Fierro and Castaldi, 2011; Karhu et al., 2015; Niboyet et al., 2011) and decreased or unaltered N_2O fluxes have been recorded (Dannenmann et al., 2011; Inclán et al., 2012; Zhao et al., 2015), most probably due to the large differences between the experiments. Several studies suggest that N_2O production in burnt soils is not closely linked with N mineralisation, as both increased N_2O production without increase in gross N rates (Karhu et al., 2015), and unaltered N_2O fluxes but increased gross N mineralisation (Dannenmann et al., 2011) have been reported. Although the factors regulating N_2O emissions in burnt soils are not clear yet, it seems that N and C availability, pH, soil moisture and temperature together with fire severity and the fire history of the site play an important role in N_2O production through denitrification (Karhu et al., 2015; Kim et al., 2011; Morishita et al., 2015). Data from Palmés fire adds evidences to the hypothesis of no direct coupling between gross N mineralisation and N_2O production, probably being the O_{NH4}/I_{NO3} ratio, net nitrification or the partitioning between DNRA and denitrification better indicators of the risk of N_2O emissions. In addition, our results point out that most certainly climatic conditions (temperature and precipitation) as well as fire severity, time since fire and plant establishment are important regulators of denitrification.

Burning and straw effects on gross N rates differ between the two experiments of this section likely due to differences in site, fire and experimental conditions. In Vilameá, under temperature and humidity conditions optimal for microbial activity, burnt soils experienced a short-lived (t=3 months) increase in MIT, especially the burnt soil without straw; a longer term (t=6 months) increase in autotrophic nitrification compared to the unburnt control; and had heterotrophic nitrification, rate that was absent in the unburnt soil. Conversely, in Palmés, the positive effect of fire on MIT in the short term was only recorded in moderately burnt soils; and in the longer term these rates only decreased in one of the burnt soils (BIM). These results could be explained by a similar fire severity in Vilaméa soils and moderately burnt Palmés soils. Another

explanation could be that the cold and very humid conditions in Palmés soils at t=3 months restricted microbial activity in the more severely burnt soils masking a positive effect of fire on MIT in these soils. The positive effect of burning on autotrophic nitrification seen in Vilameá soils was already recorded at t=3 months in Palmés soils and seemed to slightly decrease at t=6 months. Denitrification and DNRA were precluded in Vilameá soils due to the lower soil moisture (0.7x its WHC) and thus NO_3^- accumulated in all treatments (also due to the absence of plants), whereas these two processes were active in most Palmés soils. Results from the Vilameá experiment suggested that, if the conditions were favourable for denitrification, the risk of N losses through denitrification in burnt soils was rather high due to NO_3^- accumulation; and the Palmés experiment shows that highly burnt soils presented, in general, the highest denitrification rates (especially at= 6 months).

Section 7

Conclusions

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The main effects of burning 10 years after the experimental fire in Tomiño were the reduction in nitrate levels and Fe availability in soils, although no symptoms of plant Fe deficiency were detected (likely due to the iron-rich soils); and a reduced growth of the 10-year-old pines. Among the studied fire-fighting chemicals, ammonium polyphosphate was the only one which even 10 years after its application had profound effects on the ecosystem: a) increased the concentrations of soil available and plant total P; b) depressed K uptake in shrubs and increased Na uptake in legumes; c) reduced pine's viability; d) modified the species composition of the shrub community (obligate seeders hindered by resprouters); and e) played an important role in N nutrition in plants, probably by affecting their mycorrhizal (*E. umbellata* and *P. pinaster*) and rhizobial (*U. micranthus* and *P. tridentatum*) symbioses.

The field experiment after a medium-severity wildfire in a steep area (Saviñao fire) confirmed that mulching has no impact on soil and sediment concentrations of nutrients and trace elements and it does not affect net soil N rates (mineralisation and nitrification). Both soils and sediments changed with time in a similar way and it seems that the Principal Component Analyses including the studied variables can be a useful tool to assess whether burnt soils and the eroded sediments in the area are changing with time and also the speed of the change. Due to moderate precipitation rates in the experimental area that year, erosion rates were rather low and straw mulching did not have a significant effect in reducing soil erosion and the subsequent loss of nutrients. Consequently, no differences between the two mulching strategies (higher straw dose in a wide upper band and lower straw dose in alternate narrow bands) could be detected. Despite the low erosion rates, the concentrations of Mo, Mn and Zn in sediments were above reference levels for ecosystem protection.

The ^{15}N tracing experiment carried out with soil samples from Vilameá fire (preincubation in optimal conditions) shows that after 3 months of preincubation gross SON mineralisation and gross NH_4^+ immobilisation (MIT) dominated in severely burnt soils; whereas after 6 months the soil N cycle opened up and NO_3^- accumulated in burnt soils, increasing the risk of N losses. This study also shows that in optimal conditions straw mulching application, very effective in reducing post-fire erosion, had no negative impact on gross N transformation rates. Results from the Palmés experiment suggest that fire severity impacts on SOM quantity and quality and on soil microbial communities greatly affected the MIT. In the short term (t=3 months), MIT increased substantially in moderately burnt soils, whereas in highly burnt soils this increase was not recorded until t=6 months. Moreover, increased MIT combined with high soil moisture probably limited autotrophic nitrification and promoted DNRA and denitrification through competition for NH_4^+ and O_2 depletion in soil microsites. Highly burnt soils at t=6 months presented the highest denitrification rates of the whole experiment, although their low O_{NH4}/I_{NH4} ratio suggests that this high denitrification rate might not be sustained much longer. For the first time, DNRA was reported in burnt soils and it was of similar magnitude to the values reported for the unburnt control. The partitioning of NO_3^- reduction between DNRA and denitrification in burnt soils might have implications on N retention within the soil system and for greenhouse gas emissions. Straw did not have a noticeable effect in highly burnt soils, but in moderately

burnt soils mulching enhanced MIT, denitrification and DNRA, and also depressed autotrophic nitrification in the short term, probably due to the extra supply of organic matter. In the longer term, the large plants present in moderately burnt soils with mulching were probably competing with microorganisms for available N and other nutrients, and providing root exudates able to down-regulate MIT, DNRA and denitrification.

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Section 9

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Universidade de Santiago de Compostela
Departamento de Edafoloxía e Química Agrícola

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